EUROPEAN COMMISSION
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Institute for Reference Materials and Measurements

The certification of the mass concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in wastewater

BCR-713 (effluent wastewater)
BCR-714 (influent wastewater)
BCR-715 (industrial effluent wastewater

M. Segura, Y. Madrid, C. Cámara, C. Rebollo, J. Azcarate, G.N. Kramer, B.M. Gawlik, A. Lamberty, Ph. Quevauviller, S. Bowadt

Report EUR 21067

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ABSTRACT

This report describes the preparation of three spiked natural wastewater certified reference materials, i.e BCR-713 (effluent wastewater), BCR-714 (influent wastewater), BCR-715 (industrial effluent wastewater), the homogeneity and stability studies and the analytical work performed for the certification of the contents of selected trace elements. The report contains all the results and gives the methods used to certify the contents of the elements: As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in the three wastewater reference materials. The certified values in µg/L and their associated uncertainties are given in the tables below. Expanded uncertainties (coverage factor k=2) are expressed according to the Guide for the Expression of Uncertainties in Measurement (GUM).

Elements	*BCR-713*	*BCR-714*	*BCR-715*
As	9.7 ± 1.1	18.3 ± 1.6	29 ± 4
Cd	5.1 ± 0.6	19.9 ± 1.6	40 ± 5
Cr	21.9 ± 2.4	123 ± 10	$(1.00 \pm 0.09) \cdot 10^3$
Cu	69 ± 4	309 ± 23	$(0.90 \pm 0.14) \cdot 10^3$
Fe	$(0.40 \pm 0.04) \cdot 10^3$	$(1.03 \pm 0.11) \cdot 10^3$	$(3.00 \pm 0.27) \cdot 10^3$
Mn	43.4 ± 3.0	103 ± 10	248 ± 25
Ni	30 ± 5	108 ± 15	$(1.20 \pm 0.09) \cdot 10^3$
Pb	47 ± 4	145 ± 11	$(0.49 \pm 0.04) \cdot 10^3$
Se	5.6 ± 1.0	9.8 ± 1.2	29 ± 4
Zn	$(0.22 \pm 0.04) \cdot 10^3$	$(1.00 \pm 0.1) \cdot 10^3$	$(4.00 \pm 0.4) \cdot 10^3$

LIST OF ABBVREVIATIONS AND SYMBOLS

Throughout the report (including the annexes) the following abbreviations are used:

AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
AFS	Atomic Fluorescence Spectrometry
BCR	Community Bureau of Reference
BOD	Biological Oxygen Demand
CI	Confidence interval
COD	Chemical Oxygen Demand
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{ib}	Coefficient of Variation within bottle
CV_{bb}	Coefficient of Variation between bottles
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GUM	Guide for the Expression of Uncertainties in Measurement
HG	Hydride Generation
HR	High Resolution
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
MS	Mass Spectrometry
PTFE	Polytetrafluoroethylene
Q	Quadrupole
RNAA	Radiochemical Neutron Activation Analysis
s_{bb}	"true" standard deviation related to homogeneity
SD	Standard deviation
S_B	Between-laboratory standard deviation
S_W	Within-laboratory standard deviation
TIMS	Thermal Ionisation Mass Spectrometry
u_{bb}	uncertainty contribution for the inhomogeneity included in U_{CRM}
u^*_{bb}	"detection limit" for the inhomogeneity
u_{char}	uncertainty contribution for the batch characterisation included in U_{CRM}
U_{CRM}	expanded uncertainty of the certified value
U_{CV}	Uncertainty of the Coefficient of Variation
u_{lts}	uncertainty contribution for the long-term stability included in U_{CRM}
u_{sts}	uncertainty contribution for the short-term stability NOT included in U_{CRM}
WWTP	Wastewater Treatment Plant
Z	Zeeman

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1. INTRODUCTION

The European Community has decided in 1991 to oblige all Member States to be equipped with wastewater treatment plants for all cities whose wastewater organic load is greater than 15000 equivalent-inhabitants (to be implemented before Dec. 2000) and 2000 equivalent-inhabitants (to be implemented before Dec. 2005).

One of the main objectives of the new regulations related to urban and industrial waste management is to stop the direct release of sewage waters in 2002, which means that they should be treated for recycling. The physico-chemical and chemical characterisation of wastewater at the inlet (influent) and the outlet (effluent) of the treatment plants is an effective way to control the process efficiency and to verify the final quality of the effluents (Directive 91/271/EEC [1]).

From this there is an evident need for quality control of the respective water analysis, e.g. for parameters such as trace elements. Reliable results of toxic and/or non-desired analytes in waters are of crucial importance, especially when the health risk has to be assessed and actions are to be taken. Only accurate analytical data enable valid conclusions about the quality of different types of water.

Major elements can nowadays be accurately determined in natural waters in all member countries of the Commmunity. However, only a limited number of laboratories is capable of measuring with an acceptable accuracy low concentrations of toxic elements such as As, Se, Cr, Ni, Pb etc., in such a complex matrix. This lack of accuracy may be due to:

- a lack of sensitivity of the analytical method;
- interfering matrix effects which worsen the selectivity of the analysis;
- a method bias due to sample contamination or losses during sample pre-treatment and determination.

A suitable approach to identify and overcome those problems is the use of matrix CRMs and therefore the need to control the quality of these measurements requires the availability of certified reference materials representative of water matrices. The European Commission has developed through the BCR activity a range of suitable materials for quality control of water analysis such as major elements and nitrate in fresh water [2, 3], major elements in ground water [4] and rainwater [5], trace elements in estuarine and sea water [6, 7] as well as a method-dependent CRM for bromide based on IC measurements [8]. However, so far no CRM aiming at the analysis of trace elements in wastewater did exist.

This report describes the necessary feasibility study as well as the production and certification of three wastewater reference materials (BCR-713 (influent), BCR-714 (final effluent) and BCR-715 (mixed industrial effluent) for some selected trace elements, i.e. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn.

2. PARTICIPANTS

2.1 Sample preparation, homogeneity and stability studies

-	Water Treatment Plant, La China, Madrid	ES
-	European Commmision, DG JRC, Institute for Reference Materials and Measurements, Geel	BE
-	Universidad Complutense, Departamento de Química Analítica,Madrid	ES

2.2 Certification measurements

-	Aguas de Barcelona, Barcelona	ES
-	CNR, Istituo di Ricerca Sulle Acque, Brugherio	IT
-	Instituut Voor Nucleaire Wetenschappen, Gent	BE
-	Chalmers University of Technology, Göteborg	SE
-	Water Quality Institute, V.K.I, Hørsholm	DK
-	DVGW, Abteilung Analytik, Karlsruhe	DE
-	Lyonnaise des Eaux, CIRSEE, Le Pecq	FR
-	Universitat de les Illes Balears, Dept.Quimica, Mallorca	ES
-	NIVA, Norwegian Institute for Water Research, Oslo	NO
-	Lab. Chimie Analytique Bio-Organique & Environnement, UT2A, Pau	FR
-	ECN, Energie Research Foundation Nederlands, Petten	NL
-	ENEA Cassaccia, Dpto. Quimica Ambientale, Roma	IT
-	Alcontrol Laboratories, Rotherdam	UK
-	Anjou-Recherche, Lab. Central, Saint-Maurice	FR
-	Université de Bordeaux I, LPTC, Talence	FR
-	CNRS, Service Central d'Analyse, Vernaison	FR

3. PREPARATION OF THE CANDIDATE REFERENCE MATERIALS

3.1 Preliminary investigations

The optimal conditions for the preparation of wastewater candidate CRMs were tested in a feasibility study. Three batches were prepared from two spiked urban wastewater samples and a spiked industrial wastewater sample and their homogeneity was verified to evaluate possible effects of the preparation procedure on the sample composition. The stability of the test materials was also checked at –20ºC, +4ºC and +20ºC during 6 months. No significant variation with time was observed for the ten elements investigated. The study was followed by an interlaboratory study involving 16 laboratories. The results of the feasibility study are publised elsewhere [9].

3.2 Production of the materials

3.2.1 Sample collection

Urban wastewater was taken from a Wastewater Treatment Plant, WWTP, ("*La China*", Madrid, Spain) which manages the wastewater corresponding to a population of 1.3 million inhabitants. The incoming flow in this plant is practically constant (approximately 3 $m^3 s^{-1}$) which allows the sampling as a point with an important and turbulent flow. The type of treatment performed at the Wastewater Treatment Plant is conventional (pretreatment, sand removal, primary sedimentation, activated sludge process, secondary sedimentation and filtration).

The raw wastewater was collected on 26th November 1999. It was decided to take the sample in an accessible channel in which the water speed was fast enough, whereby avoiding the presence of large solids particles in the sample. Volumes of 125 litres were collected in acid cleaned polyethylene containers. This sample (raw wastewater) was called *"influent"* The other urban wastewater sample (*effluent*) was collected before the tertiary filtration stage.

The mixed industrial effluent was selected from an industrial area out of the complex network of sewers of the city. The selected sewer finishes as an open channel at the entrance of a WWTP, separately from urban wastewater, which facilitates sampling.

The medium flow of this sewer is 0.9 $m^3 s^{-1}$ and it collects the effluent of different types of industries as, for example, metallic surface treatment, food processing industries, graphic arts, etc. 125 litres were taken for the certification campaign on 30th November 1999 and stored in clean polyethylene containers (for the certification campaign this material is called *"mixed industrial effluent"*).

3.2.2 Sample preparation, homogenisation

Some general parameters were analysed to estimate the degree of pollution before applying any preparation of the sample (Table 1).

Table 1 - Analysis of the wastewater samples used for the CRM-Production

	pH	*COD* $mg\ L^{-1}$	*BOD* $mg\ L^{-1}$	*Susp. Solids* $mg\ L^{-1}$
Effluent	7.2	67	15	19
Influent	7.3	650	285	270
Mixed Industrial Effluent	6.9	830	340	350

The samples were acidified at a pH around 2 with HNO_3 and were homogenised by stirring 125 L sample volumes located in open containers to facilitate gas release during 16 h. Then they were filtered through Filtration Cartridges OPTICAP. Prefilter, pore size 1.2 µm (Millipore p.n. KW1904NP3) and though Filtrations Cartridges OPTICAP. Filter, poresize 0.5 µm (Millipore p.n. KWSC04NP3).

The filtrates were collected in clean polyethylene containers of 125 litres and were left to stand over a period of 8 months in closed containers (which were periodically opened to facilitate gas release). The adoption of this maturation stage was decided as a result of the observations made during the feasibility study about the formation of particulate matter in the filtered samples after several months of storage.

A screening analysis was done to assess the natural concentration ranges of different dissolved metals in filtered samples and it was decided to prepare spiked samples (Table 2) before the second filtration.

Table 2 - Metal target concentration ranges after spiking (µg L^{-1}) for the candidate materials.

	As	*Cd*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Se*	*Zn*
Effluent	2-15	2-15	5-30	20-100	200 -800	20-100	20-100	20-100	2-15	100-600
Influent	10-30	10-30	50-300	100-400	500-2000	50-300	50-300	50-300	5-20	800-2000
Mixed Industrial Effluent	20-50	20-80	500-2000	500-2000	2000-5000	100-500	500-2000	200-1000	20-50	3000-6000

3.2.3 Ampouling

The samples were homogenised during 1 h, under nitrogen flushing (using PTFE tubing) of the container content, using a homemade PTFE stirrer, merging in the delivered container. Filling and sealing under argon/helium mixture (90/10), of 100 mL aliquot in 120 mL capacity handmade Pyrex white glass ampoules especially designed for this project (adapted 60 mm length and 10 mm diameter for the neck and pre-opened 13 mm wide-mouthed head). The opened empty ampoules were preliminary cleaned twice with demineralized water and subsequently dried at 60 °C. The ampouling was made using the automatic filling and sealing machine of the company ROTA. During continuous homogenisation by stirring (agitator speed: ~ 40 rpm) and nitrogen flushing, the wastewater was transferred using a PTFE protected stainless steel pump connected with PTFE tubes to the 125 L container and the filling needle. Prior to ampouling, about 5 L wastewater was used to eliminate air and to rinse the tubes and pump.

The following filling and sealing procedure was used:

- Filling of a mixture of 90 % argon and 10 % helium by a filling needle;
- Filling of 100-ml wastewater by a filling needle;
- filling of a mixture of 90 % argon and 10 % helium by a filling needle;
- pre-heating of the neck of the ampoule;
- sealing of the ampoule and automatically removal of the neck of the ampoule.

4. HOMOGENEITY STUDY

The between-ampoules homogeneity was verified in 20 randomly selected ampoules of each solution (total of 60 samples) by the determination of the elements As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn without treatment. The within-ampoules homogeneity was verified by analysing one randomly chosen ampoule by 10 replicate determinations of each element in the CRMs.

4.1 Methods

The analytical methods used were Q-ICP-MS (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) and HG-AFS (Se). The samples were analysed in random order in the most repeatable manner (same day, same equipment, same person). Table 7 summarises the sample treatment and final determination followed.

4.2 Results

The homogeneity of the elements selected for certification was tested by comparing the coefficient of variation obtained within bottle (CV_{ib}) and between bottles (CV_{bb}). The estimation of the uncertainty U_{cv} of the coefficient of variations (CV) was calculated as follows:

$$U_{CV} = CV/(2n)^{1/2}$$

where n is the number of replicate determinations.

Table 3 - Results of the homogeneity tests of BCR-713, -714 and -715

Element	$CV_{ib}\pm U_{ib}$	$CV_{bb}\pm U_{bb}$	$CV_{ib}\pm U_{ib}$	$CV_{bb}\pm U_{bb}$	$CV_{ib}\pm U_{ib}$	$CV_{bb}\pm U_{bb}$
	BCR-713		*BCR-714*		*BCR-715*	
Cr	2.2±0.5	2.4±0.4	1.6±0.4	1.6±0.3	1.5±0.3	1.6±0.3
Fe	3.7±0.8	3.4±0.5	2.9±0.6	3.6±0.6	1.7±0.4	2.3±0.4
Mn	2.4±0.5	2.8±0.4	2.0±0.4	2.2±0.3	2.2±0.5	1.9±0.3
Ni	5±1	5.4±0.8	3.0±0.7	2.9±0.5	1.0±0.2	0.8±0.2
Cu	1.3±0.3	1.3±0.2	1.3±0.3	1.0±0.2	1.2±0.3	1.0±0.2
Zn	3.5±0.8	3.0±0.5	1.4±0.3	1.4±0.2	1.3±0.3	1.2±0.2
As	4.2±0.9	5.0±0.8	2.1±0.5	1.8±0.3	2.1±0.5	2.6±0.4
Se	7±2	5.0±0.8	5±1	5.1±0.8	2.7±0.6	2.4±0.4
Cd	5±1	3.9±0.6	1.5±0.3	1.2±0.2	1.3±0.3	1.5±0.2
Pb	1.9±0.4	2.3±0.4	2.9±0.7	2.2±0.4	1.6±0.4	1.3±0.2

An F-test at the significance level of 0.05 did not reveal any significant difference between the bottles and the method variances. It was hence concluded that no inhomogeneities were detected for any of the elements in the three CRMs.

An uncertainty contribution for homogeneity was included in the final uncertainty of each property value as requested by the GUM [10]. For further details refer to chapter 8.

5. STABILITY

The stability of the elements content of the three CRMs was tested to determine their suitability as reference material, by quantification of the following elements: As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn.

5.1 Method

Ampoules were kept at +4ºC, +20ºC and +40ºC, respectively, over a period of 12 months and the elements considered for the homogeneity study were determined at regular intervals during the storage period, using the same analytical procedure as for the homogeneity study. Tests were made at the beginning of the storage period, after 14 days and 1, 3, 6 and 12 months. As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn were determined by ICP-MS, As and Se by HG-AFS.

5.2 Results

Instability would be detected by comparing the contents of different elements in samples stored at different temperatures with those stored at low temperature at the various occasions of analysis. The samples stored at +4ºC were used as reference for those samples stored at +20ºC and +40ºC. Tables 4 and 5 give the ratios (R_t) of the mean values (X_t) of 5 measurements made at +20ºC and +40ºC versus the mean value ($X_{+4ºC}$) from 5 determinations made at the same occasion of analysis on samples stored at a temperature of +4ºC. The ratio was calculated as:

$$R_t = X_t / X_{+4ºC},$$

with X_t = mean of 5 replicates at temperature +20ºC and CV= coefficient of variation of 5 replicates at temperature T.

The uncertainty U_t has been obtained from the coefficient of variation (CV) of 5 measurements obtained at each temperature:

$$U_t = (CV_t^2/n + CV_{+4ºC}^{\ 2}/n)^{1/2}\ R_t$$

Tables 4 and 5 show the ratios of mean values (R_t) and the uncertainty for the elements. In case of ideal stability, R_t should be 1. In practice, however, there are some random variations due to the variability of the measurement step. In most cases the value 1 was between (R_t - U_t) and (R_t + U_t). On the basis of the results, it was concluded that no instability could be demonstrated for the tested elements. In order to establish a suitable shelf-life for each CRMs a (provisional) uncertainty contribution was estimated and included as estimate of u_{ts} into the expanded uncertainty. The expiry date could be extended once appropriate isochronous experiments are evaluated. For further explanations refer to chapter 8.

Table 4 - Stability test of BCR-713, BCR-714 and BCR-715 for As, Cd, Cu, Cr and Fe at +20ºC.

	Time (days)	*BCR-713*	*BCR-714*	*BCR-715*
As	0	0.93± 0.03	0.98± 0.02	0.98± 0.02
	14	0.96± 0.02	1.01± 0.02	0.99± 0.02
	30	1.01± 0.03	0.99± 0.02	1.00± 0.02
	90	1.00± 0.04	1.00± 0.02	1.00± 0.01
	180	1.00± 0.06	0.99± 0.02	0.96± 0.01
	360	1.00±0.03	1.01±0.02	1.01±0.01
Cd	0	1.02± 0.03	0.94± 0.02	1.00± 0.01
	14	0.98± 0.04	0.99± 0.01	1.00± 0.01
	30	1.02± 0.04	0.99± 0.02	1.02± 0.02
	90	1.02± 0.04	0.98± 0.02	1.00± 0.01
	180	1.04± 0.05	1.02± 0.02	0.98± 0.01
	360	1.10±0.05	0.98±0.02	0.99±0.01
Cu	0	0.98± 0.01	1.02± 0.01	0.99± 0.01
	14	1.01± 0.01	1.01± 0.02	1.01± 0.01
	30	1.00± 0.01	0.99± 0.01	0.99± 0.01
	90	0.97± 0.02	1.01± 0.03	1.01± 0.01
	180	0.99± 0.01	1.09± 0.01	0.97± 0.01
	360	1.03±0.01	0.98±0.02	0.99±0.01
Cr	0	0.96± 0.02	1.01± 0.02	0.98± 0.01
	14	1.02± 0.03	1.01± 0.03	1.04± 0.02
	30	1.00± 0.02	1.00± 0.02	0.99± 0.01
	90	0.99± 0.02	1.02± 0.02	0.99± 0.01
	180	0.97± 0.02	0.97± 0.01	0.98± 0.01
	360	1.00±0.02	1.01±0.01	0.98±0.02
Fe	0	1.02± 0.02	1.0± 0.02	0.99± 0.01
	14	1.05± 0.03	0.97± 0.02	0.98± 0.01
	30	0.97± 0.02	0.99± 0.02	0.97± 0.01
	90	1.04± 0.04	0.94± 0.02	0.99± 0.01
	180	1.01± 0.02	0.96± 0.01	1.00± 0.01
	360	1.00±0.06	1.01±0.01	1.01±0.01
Pb	0	1.00± 0.03	1.03± 0.02	0.97± 0.01
	14	0.98± 0.03	1.01± 0.02	1.00± 0.02
	30	0.98± 0.03	1.00± 0.01	1.01± 0.02
	90	0.98± 0.02	1.01± 0.03	1.01± 0.01
	180	1.00± 0.02	1.03± 0.01	0.99± 0.01

	Time (days)	*BCR-713*	*BCR-714*	*BCR-715*
	360	0.97±0.01	1.01±0.01	0.97±0.02
Mn	0	1.00± 0.01	1.01± 0.03	1.00± 0.01
	14	0.99± 0.01	1.02± 0.04	1.01± 0.02
	30	0.99± 0.01	1.00± 0.03	1.04± 0.02
	90	0.99± 0.01	1.05± 0.04	1.00± 0.02
	180	1.00± 0.01	1.02± 0.01	0.99± 0.01
	360	1.02±0.02	1.01±0.01	0.99±0.01
Ni	0	0.96± 0.06	1.01± 0.03	0.99± 0.01
	14	0.96± 0.05	1.02± 0.03	0.98± 0.01
	30	1.04± 0.08	0.98± 0.02	1.01± 0.01
	90	1.04± 0.09	1.02± 0.02	0.99± 0.01
	180	0.93± 0.07	1.04± 0.02	0.98± 0.01
	360	1.03±0.03	1.01±0.02	1.01±0.01
Se	0	1.00± 0.05	0.99± 0.05	0.99± 0.01
	14	1.02± 0.06	1.04± 0.04	1.03± 0.02
	30	1.00± 0.06	1.00± 0.04	1.02± 0.02
	90	1.05± 0.07	1.01± 0.02	0.96± 0.01
	180	1.09± 0.05	0.93± 0.05	1.07± 0.04
	360	1.04±0.04	0.96±0.02	0.95±0.01
Zn	0	0.93± 0.04	1.00± 0.02	0.99± 0.01
	14	0.93± 0.01	0.98± 0.02	1.00± 0.01
	30	1.05± 0.03	1.01± 0.02	0.98± 0.01
	90	1.09± 0.06	1.01± 0.02	1.01± 0.01
	180	1.04± 0.03	0.98± 0.01	0.96± 0.01
	360	0.99±0.02	0.98±0.01	1.01±0.01

Table 5 - Stability test of BCR-713, BCR-714 and BCR-715 for As, Cd, Cu, Cr and Fe at +40ºC.

	Time (days)	*BCR-713*	*BCR-714*	*BCR-715*
As	0	0.95± 0.02	0.98± 0.02	0.98± 0.02
	14	0.98± 0.02	0.99± 0.02	0.99± 0.02
	30	1.01± 0.03	1.04± 0.02	1.01± 0.02
	90	0.99± 0.03	0.99± 0.02	1.01± 0.02
	180	1.03± 0.05	1.00± 0.02	1.02± 0.02
	360	1.06±0.04	1.01±0.02	0.99±0.01
Cd	0	0.96± 0.03	0.96± 0.02	1.00± 0.01
	14	1.02± 0.04	0.99± 0.01	1.00± 0.01
	30	1.02± 0.05	0.98± 0.02	1.02± 0.02
	90	1.00± 0.04	1.00± 0.02	0.99± 0.01
	180	1.04± 0.02	1.06± 0.02	1.01± 0.01
	360	1.02±0.04	1.01±0.02	0.99±0.01
Cu	0	1.00± 0.01	1.01± 0.02	0.99± 0.01
	14	1.00± 0.01	0.98± 0.02	1.01± 0.01
	30	1.01± 0.01	0.99± 0.02	1.00± 0.01
	90	1.00± 0.02	1.02± 0.02	1.03± 0.01
	180	1.00± 0.01	1.00± 0.02	0.92± 0.01
	360	1.00±0.01	1.00±0.01	0.99±0.01
Cr	0	0.95± 0.01	1.00± 0.02	1.01± 0.02
	14	1.00± 0.02	0.98± 0.03	1.01± 0.01
	30	0.99± 0.02	1.00± 0.01	1.00± 0.02
	90	1.00± 0.02	1.01± 0.03	0.99± 0.01
	180	1.01± 0.02	0.98± 0.01	1.01± 0.01
	360	1.01±0.04	0.99±0.01	1.01±0.02
Fe	0	1.01± 0.02	1.03± 0.01	1.00± 0.01
	14	1.06± 0.03	0.97± 0.02	0.99± 0.01
	30	0.98± 0.02	1.00± 0.01	1.04± 0.01
	90	1.08± 0.04	0.95± 0.02	0.99± 0.01
	180	1.11± 0.01	1.06± 0.02	0.97± 0.01
	360	1.07±0.05	1.01±0.02	1.00±0.01
Pb	0	0.95± 0.03	0.99± 0.02	0.98± 0.01
	14	1.05± 0.03	1.00± 0.02	1.01± 0.02
	30	1.05± 0.02	0.96± 0.02	1.00± 0.02
	90	1.00± 0.02	1.02± 0.03	0.99± 0.01
	180	1.00± 0.03	1.01± 0.02	1.00± 0.01
	360	0.94±0.01	0.99±0.02	0.97±0.02

	Time (days)	*BCR-713*	*BCR-714*	*BCR-715*
Mn	0	0.98± 0.01	1.02± 0.04	0.99± 0.01
	14	0.98± 0.01	1.01± 0.04	0.99± 0.02
	30	0.98± 0.01	1.07± 0.03	1.04± 0.02
	90	1.00± 0.01	1.05± 0.04	1.00± 0.02
	180	1.03± 0.01	0.97± 0.01	1.01± 0.01
	360	1.01±0.02	1.00±0.02	1.00±0.01
Ni	0	1.04± 0.07	1.05± 0.02	0.98± 0.01
	14	1.00± 0.06	1.03± 0.03	1.02± 0.01
	30	0.96± 0.08	0.98± 0.03	1.00± 0.01
	90	1.08± 0.09	1.04± 0.03	1.01± 0.01
	180	0.97± 0.05	1.02± 0.04	1.02± 0.01
	360	1.07±0.04	1.02±0.01	1.00±0.02
Se	0	1.00± 0.05	0.97± 0.05	1.03± 0.01
	14	1.00± 0.06	1.02± 0.04	1.03± 0.02
	30	1.00± 0.06	1.00± 0.04	1.03± 0.02
	90	1.02± 0.07	1.02± 0.02	0.95± 0.01
	180	1.02± 0.05	0.90± 0.04	1.00± 0.04
	360	1.02±0.04	0.98±0.02	0.98±0.01
Zn	0	1.06± 0.05	0.97± 0.02	1.00± 0.01
	14	0.92± 0.02	0.97± 0.02	1.00± 0.01
	30	1.03± 0.03	1.01± 0.03	0.98± 0.01
	90	1.03± 0.07	0.96± 0.02	1.02± 0.01
	180	1.00± 0.03	1.02± 0.01	0.99± 0.01
	360	1.05±0.02	0.97±0.01	1.02±0.01

6. METHODS USED FOR THE CERTIFICATION EXERCISE

Each laboratory that took part in the certification campaign was requested to make a minimum of six independent replicate determinations of each element on at least two different bottles of the three CRMs on two different days without mineralising the samples. Each set of results is identified by the code number of the laboratory. Methodology and techniques used by each participant are described in Tables 6 – 15.

To obtain the accuracy and the reliability required for certification it is necessary to ensure that no substantial systematic error is left undetected. For this purpose some considerations were taken into account. The laboratories participating in the certification exercise applied their methods correctly. They used at least the following quality control steps:

- The determinations were performed only when the method was under control.
- Whenever possible, analytical methodology was validated by analysing available reference materials.

The considerations presented in Tables 6 - 15 and the evidence given by the bar-graphs (Annex I), led to the conclusion that there was no substantial difference between the methods and that therefore the probability of systematic error would be low.

Table 6 - Summary of the methods for final determination of Arsenic

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: reduction with $NaBH_4$ in acid mixture; Calibrant: commercial solution of As in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3103 a; external calibration graph with independent control point	HG-AAS at 193.7 nm	01
Pretreatment: addition of Rh as internal standard; Calibrant: As in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3103 a, use of SRM 1643 d; external calibration graph	ICP-MS of ^{75}As	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of As in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3103 a; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{75}As	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of As in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3103 a; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 193.696 nm	04
Pre-treatment: addition of In as internal standard; Calibrant: commercial H_3AsO_4 solution in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3103 a; external calibration graph	HR-ICP-MS of ^{75}As	05
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: commercial solution of As in 1 mol L^{-1} HNO_3 (Alfa), traceable to NIST SRM 3103a; standard addition calibration graph	HR-ICP-MS of ^{75}As (R: 7500)	06
Pre-treatment: addition of $Ni(NO_3)_2$ modifier; Calibrant: commercial solution of As (V) in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3103; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 193.7 nm	08
Pre-treatment: reduction with 1 mol L^{-1} $NaBH_4$ and 0.25 mol L^{-1} NaOH in 1 mol L^{-1} HCl, 0.9 mol L^{-1} KI; Calibrant: commercial solution of As in 1 mol L^{-1} HNO_3 (PerkinElmer); standard addition calibration graph	HG-AAS at 193.7 nm	09a
Pre-treatment: addition of Pd+ $Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of As in 1 mol L^{-1} HNO_3 (PerkinElmer); standard addition calibration graph	ZETAAS at 193.7 nm	09b
Pre-treatment: reduction with 0.2 mol L^{-1} $NaBH_4$ in 0.1 mol L^{-1} NaOH. Samples matched to a 10.7 mol L^{-1} HCl matrix, 3 mol L^{-1} KI and 0.6 mol L^{-1} ascorbic acid; Calibrant: multi-element standard solution in 1 mol L^{-1} HNO_3 (QMX), traceabe to NIST SRM 3103 a; use of external calibration graph in 0.2 mol L^{-1} HNO_3 and 0.026 mol L^{-1} HF	HG-AFS 193.7 nm	10
No pre-treatment; Calibrant: commercial solution of As in 0.5 mol L^{-1} HNO_3, (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{75}As	11
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3103 a, use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{75}As	13

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: reduction with 0.8 mol L^{-1} $NaBH_4$ in 0.25 mol L^{-1} NaOH in 6 mol L^{-1} HCl; Calibrant: commercial solution of As_2O_5 in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3103 a; external calibration graph	HG-AFS 193.7 nm	14a
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of As_2O_5 in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3103 a; external calibration graph	ICP-MS of ^{75}As	14b
Pre-treatment: gravimetric, radiochemical separation: Ion exchange on HMD; irradiation for 4 hours at a flux of $3x10^{11} cm^{-2}s^{-1}$, decay time 4 days, counting time 4-24 h. Calibrant: NIST 3172 A	RNAA	15
Pre-treatment: volumetric dilution, reduction with 0.05 mol L^{-1} $NaBH_4$ in 0.01 mol L^{-1} NaOH, 0.3 mol L^{-1} KI and 0.3 mol L^{-1} ascorbic acid; Calibrant: commercial solution of As (V) in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3103 a; external calibration graph	HG-ETAAS at 193.7 nm	16
No pre-treatment; Calibrant: commercial solution of As in 1 mol L^{-1} $HNO_3$1 mol L^{-1} HNO_3 (Alfa), traceable to NIST SRM 3103 a; external calibration graph and standard addition calibration graph	ICP-AES at 189.0 nm	17

Table 7 - Summary of the methods for final determination of Cadmium

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Cd in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108; external calibration graph with independent control point	ICP-AES at 228.8 nm	01
Pretreatment: volumetric dilution, addition of Rh as internal standard; Calibrant: solution of $Cd(NO_3)_3$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108, use of SRM 1643 d; external calibration graph	ICP-MS of ^{111}Cd	02
Pre-treatment: volumetric dilution; addition of Rh as internal standard; Calibrant: commercial solution of Cd in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3108; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{112}Cd	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Cd in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 226.5 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of Cd in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3108; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 214.4 nm	05a
Pre-treatment: addition of In as internal standard; Calibrant: commercial (SPEX) solution of Cd in 0.4 mol L^{-1} HNO_3; traceable to NIST SRM 3108; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-MS of ^{111}Cd, ^{112}Cd	05b
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108; standard addition calibration graph	HR-ICP-MS of ^{114}Cd (R: 300)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cd in 0.24 mol L^{-1} (Merck), traceable to NIST SRM 3108; calibration graph in 0.2 mol L^{-1} HNO_3.	ICP-AES at 228.8 nm	07
No Pre-treatment; Calibrant: commercial solution of Cd in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 228.8 nm	08
No Pre-treatment; Calibrant: commercial solution of Cd in 1 mol L^{-1} HNO_3 (PerkinElmer), traceable to NIST SRM 3108; external calibration graph	FAAS at 228.8 nm	09a
Pre-treatment: volumetric dilution; addition of $NH_4H_2PO_4$+ $Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of Cd in 1 mol L^{-1} HNO_3 (PerkinElmer), traceable to NIST SRM 3108; external calibration graph	ZETAAS at 228.8 nm	09b
No pre-treatment; Calibrant: multi-element standard solution (QMX), traceable to NIST 3108; external calibration graph	ICP-AES at 214.4 nm	10a
Pre-treatment: addition of Rh as internal standard; Calibrant: multi-element standard solution (QMX), traceable to NIST 3108; external calibration graph	ICP-MS of ^{111}Cd	10b
No pre-treatment; Calibrant: Commercial solution of Cd in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{111}Cd	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cd in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST 3108; external calibration graph	ICP-MS of ^{114}Cd and ^{115}Cd	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard solution in 1 mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3108; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{111}Cd	13

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Cd in 0.4 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3108; external calibration graph	ICP-MS of ^{111}Cd	14
Pre-treatment: gravimetric, radiochemical separation: Ion exchange on Chelex; irradiation for 4 hours at a flux of $3x10^{11}cm^{-2}s^{-1}$, decay time 4 days, counting time 4 to 24 hours; Calibrant: NIST 3171 a	RNAA	15
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cd $(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3108; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 228.8 nm	16
No Pre-treatment; Calibrant: commercial solution of Cd in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3108; external calibration graph and standard addition calibration graph	ICP-AES at 214.4 nm	17

Table 8 - Summary of the methods for final determination of Copper

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Cu in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3114; external calibration graph with independent control point	ICP-AES at 324.8 nm	01
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of $Cu(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3114; use of SRM 1643 d; external calibration graph	ICP-MS of ^{63}Cu	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Cu in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3114; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS in ^{63}Cu	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Cu in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3114; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 324.8 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of Cu in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3114; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 214.4 nm	05a
Pre-treatment: volumetric solution, addition of In as internal standard; Calibrant: commercial solution of Cu (SPEX) in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3114; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-MS of ^{63}Cu and ^{65}Cu	05b
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution in 1 mol L^{-1} HNO_3 (Merck), traceabe to NIST SRM 3114; standard addition calibration graph	HR-ICP-MS of ^{63}Cu and ^{65}Cu (R: 3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cu in 0.2 mol L^{-1} (Merck), traceabe to NIST SRM 3114; external calibration graph in 0.2 mol L^{-1} HNO_3.	ICP-AES at 324.8 nm	07
No pre-treatment; Calibrant: commercial solution of Cu in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3114; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 324.8 nm	08
No pre-treatment; Calibrant: commercial solution of Cu in 1 mol L^{-1} HNO_3 (PerkinElmer), traceabe to NIST SRM 3114; external calibration graph	FAAS at 324.8 nm	09a
Pre-treatment: volumetric dilution; addition of Pd+ $Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of Cu in 1 mol L^{-1} HNO_3 (PerkinElmer), traceabe to NIST SRM 3114; external calibration graph	ZETAAS at 324.8 nm	09b
No pre-treatment; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3114; external calibration graph	ICP-AES at 327.4 nm	10a
Pre-treatment: addition of Sc as internal standard; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3114; external calibration graph	ICP-MS of ^{65}Cu	10b
No pre-treatment; Calibrant: commercial solution of Cu in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{63}Cu	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cu in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST SRM 3114; external calibration graph	ICP-MS of ^{63}Cu and ^{65}Cu	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard in 1 mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3114; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{65}Cu	13

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Cu(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceabe to NIST SRM 3114; external calibration graph	ICP-MS of ^{63}Cu and ^{65}Cu	14
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Cu(NO_3)_2.3H_2O$ in 0.05 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3114; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 228.8 nm	16
No pre-treatment; Calibrant: commercial solution of Cu in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3114; external calibration graph and standard addition calibration graph	ICP-AES at 327.4 nm	17

Table 9 - Summary of the methods for final determination of Chromium

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Cr in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3112 a; external calibration graph with independent control point	ICP-AES at 267.7 nm	01
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of Cr $(NO_3)_3$ in 0.4 mol L^{-1} HNO_3 (Perkin Elmer), traceable to NIST SRM 3112 a; use of SRM 1643 d; external calibration graph	ICP-MS of ^{52}Cr	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of Cr in 1.6 mol L^{-1} HCl (Techlab), traceable to NIST SRM 3112 a; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{52}Cr	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Cr in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3112 a; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 205.6 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of $Cr(NO_3)_3$ in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3112 a; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 205.6 nm	05a
Pre-treatment: volumetric dilution, addition of In as internal standard; Calibrant: commercial (SPEX) solution of $Cr(NO_3)_3$ in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3112 a; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-MS of ^{52}Cr	05b
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution in 1 mol L^{-1} HNO_3 (Merck); traceable to NIST SRM 3112 a; standard addition calibration graph	HR-ICP-MS of ^{52}Cr (R: 3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution from K_2CrO_4 in 0.2 mol L^{-1} (Panreac); external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 267.7 nm	07
No pre-treatment; Calibrant: commercial solution of Cr in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3112 a; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 267.7 nm	08
No pre-treatment; Calibrant: commercial solution of Cr in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 357.9 nm	09a
Pre-treatment: volumetric dilution; addition of $Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of Cr in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	ZETAAS at 357.9 nm	09b
No pre-treatment; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3 traceable to NIST SRM 3112 a; external calibration graph	ICP-AES at 267.7 nm	10a
Pre-treatment: addition of Sc as internal standard; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3112 a; external calibration graph	ICP-MS of ^{52}Cr	10b
No pre-treatment; Calibrant: commercial solution of Cr in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{52}Cr and ^{53}Cr	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Cr in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST SRM 3112 a; external calibration graph	ICP-MS of ^{52}Cr and ^{53}Cr	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard in 1mol L^{-1} HNO_3 (Accustandard); traceable to NIST SRM 3112 a; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{52}Cr	13
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Cr(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3112 a; external calibration graph	ICP-MS of ^{52}Cr and ^{53}Cr	14
Pre-treatment: gravimetric, radiochemical separation: Ion exchange on Chelex; irradiation for 4 hours at a flux of $3x10^{11}cm^{-2}s^{-1}$, decay time 4 days, counting time 4 to 24 hours Calibrant: NIST 3171 A	RNAA	15
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Cr(NO_3)_3$ in 0.05 mol L^{-1} HNO_3 (Fluka Chemika), traceabe to NIST SRM 3112 a; external calibration graph in 0.1 mol L^{-1}	ETAAS at 357.9 nm	16

Sample pre-treatment	*Final determination*	*Lab. Code*
HNO_3		
No pre-treatment; Calibrant: commercial solution of Cr in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3112 a; external calibration graph and standard addition calibration graph	ICP-AES at 267.7 nm	17

Table 10 - Summary of the methods for final determination of Iron

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Fe(III) in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; external calibration graph with independent control point	ICP-AES at 259.9 nm	01
Pre-treatment: volumetric dilution, addition of Yb as internal standard; Calibrant: aqueous solution of Fe_2O_3 in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; use of SRM 1643 d; external calibration graph	ICP-AES at 238.2 nm	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Fe in 0.4 mol L^{-1} HNO_3 (Merck); use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{57} Fe	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Fe in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 259.9 nm	04
No pre-treatment; Calibrant: commercial solution of $Fe(NO_3)_3$ in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3126 a; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 259.9 nm	05
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; standard addition calibration graph	HR-ICP-MS of ^{56}Fe (R: 3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Fe(NH_4) $(SO_4)_2$ in 0.6 % H_2SO_4(Panreac); external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 259.9 nm	07
No pre-treatment; Calibrant; commercial solution of Fe in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 259.9 nm	08
No pre-treatment; Calibrant: commercial solution of Fe in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 248.3 nm	09a
No pre-treatment; Calibrant: commercial solution of Fe in 1mol L^{-1} HNO_3 (BDH), traceable to NIST SRM 3126 a; external calibration graph	ICP-AES at 238.2 nm	10
No pre-treatment; Calibrant: commercial solution of Fe in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; use of NRC SLRS-3; external calibration graph	GF-AAS at 248.3 nm	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Fe (Alfa/ JM); external calibration graph	ICP-MS of ^{57}Fe	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard solution in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST CRM 3126; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{57}Fe	13
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Fe(NO_3)_3$ in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; external calibration graph	ICP-MS of ^{57}Fe	14
Pre-treatment: gravimetric, radiochemical separation: Ion exchange on chelex; irradiation for 4 hours at a flux of $3x10^{11}cm^{-2}s^{-1}$, decay time 4 days, counting time 4 to 24 hours; Calibrant: NIST 3171 A	RNAA	15
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Fe(NO_3)_3$ in 0.05 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3126 a; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 248.3 nm	16
No pre-treatment; Calibrant: commercial solution of Fe in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3126 a; external calibration graph and standard additions calibration grahp	ICP-AES at 238.2 nm	17

Table 11 - Summary of the methods for final determination of Lead

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph with independent control point	ICP-AES at 220.3 nm	01
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of Pb in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128, use of SRM 1643 d; external calibration graph	ICP-MS of ^{208}Pb	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Pb in 0.4 mol L^{-1} HNO_3 (Baker), traceable to NIST SRM 3128; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{208}Pb	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Pb in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 220.3 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of $Pb(NO_3)_2$ in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3128; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 220.3 nm	05a
Pre-treatment: volumetric dilution, addition of In as internal standard; Calibrant: commercial solution of $Pb(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3128; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-MS of ^{206}Pb, ^{207}Pb, ^{208}Pb	05b
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of Tl as internal standard; Calibrant: multi-element standard in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; calibration standard addition graph	HR-ICP-MS of ^{208}Pb (R:300)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Pb(NO_3)_2$ in 0.2 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 220.3 nm	07
No pre-treatment; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 220.3 nm	08a
No pre-treatment; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 220.3 nm	08b
No pre-treatment; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 217.0 nm	09a
Pre-treatment: volumetric dilution; addition of $NH_4H_2PO_4$+$Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	ZETAAS at 217.0 nm	09b
No pre-treatment; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3128; external calibration graph	ICP-AES at 220.3 nm	10a
Pre-treatment; addition of Bi as internal standard; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3128; external calibration graph	ICP-MS of ^{208}Pb	10b
No pre-treatment; Calibrant: commercial solution of Pb in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of SLRS-3; external calibration graph	ICP-MS of ^{208}Pb	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Pb in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST 3128; external calibration graph	ICP-MS of ^{206}Pb and ^{208}Pb	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard solution in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3128; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{208}Pb	13
Pre-treatment: volumetric dilution, addition of Tl as internal standard; Calibrant: commercial solution of $Pb(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph	ICP-MS of ^{206}Pb and ^{208}Pb	14
Pre-treatment: gravimetric dilution; Calibrant: solution of Pb-spike; IDMS in reversed mode to calibrate Pb-spike. Calibrant: NIST SRM 49 e	TIMS of ^{206}Pb, ^{207}Pb and ^{208}Pb	15
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Pb(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3128; calibration standard addition graph	ETAAS at 283.3 nm	16
No pre-treatment; Calibrant: commercial solution of Pb in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3128; external calibration graph and standard addition calibration graph	ICP-AES at 220.3 nm	17

Table 12 - Summary of the methods for final determination of Manganese

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Mn in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132; external calibration graph	ICP-AES at 257.6 nm	01
Pre-treatment: volumetric dilution, addition of Yb as internal standard; Calibrant: aqueous solution of $Mn(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132, use of SRM 1643 d; external calibration graph	ICP-AES at 257.6 nm	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Mn(C_2H_3O_2)_2$ in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST 3132; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS ^{55}Mn	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Mn in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 257.6 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of $Mn(C_2H_3O_2)_2$ in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3132; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 257.6 nm	05
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132; standard addition calibration graph	HR-ICP-MS of ^{55}Mn (R:3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Mn in 0.3 mol L^{-1} HCl (Merck), traceable to NIST SRM 3132; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 257.6 nm	07
No pre-treatment; Calibrant: commercial solution of Mn in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 257.6 nm	08
No pre-treatment; Calibrant: commercial solution of Mn in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 279.5 nm	09a
Pre-treatment: volumetric dilution; addition of Pd+$Mg(NO_3)_2$ as modifier; Calibrant: commercial solution of Mn in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	ZETAAS at 279.5 nm	09b
No pre-treatment; Calibrant: multi-element standard solution (QMX) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3132; external calibration graph	ICP-AES at 257.6 nm	10a
Pre-treatment; addition of Sc as internal standard; Calibrant: multi-element standard solution (QMX) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3132; external calibration graph	ICP-MS of ^{55} Mn	10b
No pre-treatment; Calibrant: commercial solution of Mn in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{55}Mn	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Mn (Alfa /JM); external calibration graph	ICP-MS of ^{55}Mn	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard solution in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST CRM 3132; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{55}Mn	13
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Mn(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3132; external calibration graph	ICP-MS of ^{55}Mn	14
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Mn(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3132; external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 279.5 nm	16
No pre-treatment; Calibrant: commercial solution of Mn in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3132; external calibration graph and standard additions calibration graph	ICP-AES at 257.6 nm	17

Table 13 - Summary of the methods for final determination of Nickel

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3136; external calibration graph	ICP-AES at 231.6 nm	01
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of $Ni(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136, use of SRM 1643 d; external calibration graph	ICP-MS of ^{60}Ni	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3136; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{58}Ni	03

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Ni in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 231.6 nm	04
No pre-treatment; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3136; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 231.6 nm	05a
Pre-treatment: volumetric dilution, addition of In as internal standard; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3136; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-MS of ^{60}Ni	05b
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136; standard addition calibration graph	HR-ICP-MS of ^{58}Ni-^{60}Ni (R: 3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Ni in 0.2 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 231.6 nm	07
No pre-treatment; Calibrant: commercial solution of Ni in 1mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 231.6 nm	08
No pre-treatment; Calibrant: commercial solution of Ni in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 232.0 nm	09a
Pretreatment: volumetric dilution; Calibrant: commercial solution of Ni in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	ZETAAS at 232.0 nm	09b
No pre-treatment; Calibrant: multi-element standard solution in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3136; external calibration graph	ICP-AES at 231.6 nm	10a
Pre-treatment: addition of Sc as internal standard; Calibrant: multi-element standard solution in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3136; external calibration graph	ICP-MS of ^{60}Ni	10b
No pre-treatment; Calibrant: commercial solution of Ni in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{60}Ni	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST 3136; external calibration graph	ICP-MS of ^{58}Ni	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard solution in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3136; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{62}Ni	13
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Ni in 0.4 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3136; external calibration graph	ICP-MS of ^{60}Ni and ^{62}Ni	14
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Ni(NO_3)_2$ in 0.05 mol L^{-1} HNO_3 (Fluka Chemika); external calibration graph in 0.1 mol L^{-1} HNO_3	ETAAS at 232.0 nm	16
No pre-treatment; Calibrant: commercial solution of Ni in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3136; external calibration graph and standard additions calibration grahp	ICP-AES at 216.5 nm	17

Table 14 - Summary of the methods for final determination of Selenium

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: addition of $Ni(NO_3)_2$ matrix modifier; Calibrant: commercial solution of Se in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149; external calibration graph with independent control point	ZETAAS at 196.0 nm	01
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: aqueous solution of SeO_2 in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149, use of SRM 1643 d; external calibration graph	ICP-MS of ^{82}Se	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Se in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3149; use of SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{82}Se	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Se in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 196.0 nm	04
Pre-treatment: addition of In as internal standard; Calibrant: commercial solution of Se in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3149; external calibration graph in 0.4 mol L^{-1} HNO_3	HR-ICP-MS of ^{82}Se	05
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard;	ICP-MS of ^{82}Se	06

Sample pre-treatment	*Final determination*	*Lab. Code*
Calibrant: commercial solution of Se in 1 mol L^{-1} HNO_3 (Alfa Aesar), traceable to NIST SRM 3149; standard addition calibration graph		
No pre-treatment; Calibrant: commercial solution of Se in 0.4 mol L^{-1} HNO_3 (SPEX), traceable to NIST SRM 3149; calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 196.1 nm	08
Pre-treatment: pre-reduction with 4 mol L^{-1} HCl (1:1), derivatization with 1 mol L^{-1} $NaBH_4$ in 0.25 mol L^{-1} NaOH in 1 mol L^{-1} HCl; Calibrant: commercial solution of Se in 1 mol L^{-1} HNO_3 (PerkinElmer); standard addition calibration graph	HG-AAS at 196.0 nm	09
Pre-treatment: pre-reduction with HCl and H_2O_2, derivatization with 0.2 mol L^{-1} $NaBH_4$ in 0.1 mol L^{-1} NaOH; Calibrant: multi-element standard solution (QMX) in 3.2 mol L^{-1} HCl, traceable to NIST SRM 3149; external calibration graph	HG-AFS at 196.0 nm	10
No pre-treatment; Calibrant: commercial solution of Se in 0.5 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149; use of SLRS-3; external calibration graph	ICP-MS of ^{78}Se and ^{82}Se	11
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST SRM 3149; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{82}Se	13
Pre-treatment: pre-reduction in 6 mol L^{-1} HCl, derivatization with 0.3 mol L^{-1} $NaBH_4$ in 0.075 mol L^{-1} NaOH; Calibrant: commercial solution of Se (IV) in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149; external calibration graph	HG-AFS at 196.0 nm	14
Pre-treatment: gravimetric, radiochemical separation: Ion exchange on HMD; irradiation for 4 hours at a flux of $3x10^{11}cm^{-2}s^{-1}$, decay time 4 days, counting time 4 to 24 hours Calibrant: NIST SRM 726	RNAA	15
Pre-treatment: pre-reduction in 6 mol L^{-1} HCl; derivatization with 0.05 mol L^{-1} $NaBH_4$ in 0.01 mol L^{-1} NaOH; Calibrant: solution of Se prepared from Na_2SeO_4 (Aldrich); external calibration graph	HG-ETAAS at 196.0 nm	16
No pre-treatment; Calibrant: commercial solution of Se in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3149; external calibration graph and standard addition graph	ICP-AES at 196.0 nm	17

Table 15 - Summary of the methods for final determination of Zinc

Sample pre-treatment	*Final determination*	*Lab. Code*
No pre-treatment; Calibrant: commercial solution of Zn in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168 a; external calibration graph with independent control point	ICP-AES at 213.9 nm	01
Pre-treatment: addition of Rh as internal standard; Calibrant: aqueous solution of $Zn(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168 a, use of SRM 1643 d; external calibration graph	ICP-MS of ^{66}Zn	02
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of Zn in 0.4 mol L^{-1} HNO_3 (Techlab), traceable to NIST SRM 3168 a; use of NRCC SLRS-2, SLRS-3, SRM 1643 d; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-MS of ^{66}Zn	03
Pre-treatment: addition of HNO_3 to pH=1; Calibrant: commercial solution of Zn in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168 a; use of NIST 1640; calibration graph in matrix matching of Na, K, Ca and Mg	ICP-AES at 213.9 nm	04
No pre-treatment; Calibrant: commercial (SPEX) solution of Zn in 0.4 mol L^{-1} HNO_3, traceable to NIST SRM 3168 a; external calibration graph in 0.4 mol L^{-1} HNO_3	ICP-AES at 213.9 nm	05
Pre-treatment: volumetric dilution with 0.14 mol L^{-1} HNO_3, addition of In as internal standard; Calibrant: 11355 multi-element standard solution in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168 a; standard addition calibration graph	HR-ICP-MS of ^{66}Zn, ^{68}Zn (R:3000)	06
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Zn; in 0.3 mol L^{-1} HCl (Merck), traceable to NIST SRM 3168 a; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-AES at 206.0 nm	07
No pre-treatment; Calibrant: commercial solution of Zn in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3168 a; external calibration graph in 0.1 mol L^{-1} HNO_3	ICP-AES at 231.6 nm	08
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Zn in 1 mol L^{-1} HNO_3 (PerkinElmer); external calibration graph	FAAS at 213.9 nm	09
No pre-treatment; Calibrant: multi-element standard solution in 1 mol L^{-1} HNO_3 (CPI), traceable to NIST SRM 3168 a; external calibration graph	ICP-AES at 213.8 nm	10a

Sample pre-treatment	*Final determination*	*Lab. Code*
Pre-treatment: addition of Rh as internal standard; Calibrant: multi-element standard solution (CPI) in 1 mol L^{-1} HNO_3, traceable to NIST SRM 3168 a; external calibration graph	ICP-MS of ^{66}Zn	10b
No pre-treatment; Calibrant: commercial solution of Zn in 0.5 mol L^{-1} HNO_3 (Spectrascan); use of NRC SLRS-3; external calibration graph	ICP-MS of ^{66}Zn	11
Pre-treatment: volumetric dilution; Calibrant: commercial solution of Zn in 0.4 mol L^{-1} HNO_3 (HPS), traceable to NIST 3168; external calibration graph	ICP-MS of ^{64}Zn and ^{66}Zn	12
Pre-treatment: gravimetric dilution; Calibrant: commercial multi-element standard in 1mol L^{-1} HNO_3 (Accustandard), traceable to NIST CRM 3168 a; use of NRCC SLRS-3; external calibration graph in 0.2 mol L^{-1} HNO_3	ICP-MS of ^{66}Zn	13
Pre-treatment: volumetric dilution, addition of Rh as internal standard; Calibrant: commercial solution of $Zn(NO_3)_2$ in 0.4 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168; external calibration graph	ICP-MS of ^{66}Zn	14
Pre-treatment: volumetric dilution; Calibrant: commercial solution of $Zn(NO_3)_2$ in 0.5 mol L^{-1} HNO_3 (Fluka Chemika), traceable to NIST SRM 3168 a; external calibration graph in 0.1 mol L^{-1} HNO_3	FAAS at 213.9 nm	16
No pre-treatment; Calibrant: commercial solution of Zn in 1 mol L^{-1} HNO_3 (Merck), traceable to NIST SRM 3168; external calibration graph and standard addition calibration graph	ICP-AES at 213.9 nm	17

7. TECHNICAL AND STATISTICAL DISCUSSION

The data obtained by all participants (see Annex I) were presented in the form of "*bar-graphs*" including the laboratory code with the analytical technique used, the mean of all individual values with the corresponding standard deviation and the mean of the mean values with its corresponding standard deviation. All the results were discussed at a technical evaluation meeting to confirm the accuracy of the method of analysis. The attendance of the participants to the meeting was considered to be a prerequisite for acceptance of results for certification; in case of suspicion thrown on a set of data of an absent participant (hence without the possibility to discuss the results on technical ground), the set was automatically rejected. The conclusions and general or particular comments on results at the technical certification meeting were as follows:

The results provided by participants who were not able to demonstrate their traceability (lack of confidence on the calibrants, suspicious of losses or contamination) were not considered for certification (Lab 13 for all the elements).

The main problems discussed in the certification meeting (rejected values) were due to:

- Too large standard deviation: Lab 01 (Zn in BCR-714), Lab 10 (Ni in BCR-713), Lab 15 (Fe in BCR-715) and Lab 17 (As in all BCRs);
- Too low standard deviation (not considered realistic): Lab 09 (Se in BCR-713 and BCR-714) ;
- Systematic errors or contamination problems: Lab 09 (Cr in all BCRs; Mn, Zn and Ni in BCR-713), Lab 05 (Se in BCR-714 and BCR-715) and Lab 16 (Zn in BCR-713) ;
- Calibrant problems: Lab 03 (As, Cd, Cr, Cu, Ni. Pb and Zn) ;
- Discrepancy of results at different days: Lab 07 (Zn in BCR-713) ;
- Discrepancy of results when two different techniques were used by the same participant: Lab 09 (As, Cd, Cu in all CRMs and Ni in BCR-714) ;
- Close to the detection limit: Lab 16 (Fe in BCR-713) and Lab 17 (Se in BCR-713 and BCR-714).

After discussion, only ICP-AES results for Cr from Lab 10 were accepted because of the lack of confidence of the results obtained using ICP-MS. Data obtained by Lab 12 for Cr were lower than the mean of the means in all cases, but they were included because no scientific reasons justify the rejection of the set of data.

The rest of results that were provided by the participants for the three CRMs (BCR-713, BCR-714 and BCR-715), were included for certification, because they fulfill the requirements for this purpose.

7.1 General statistical discussion

For each set of results the mean value and the standard deviation have been calculated. All the results are presented in form of "*bar-charts*" in Annex I.

The sets of results have been subjected to the following statistical tests:

- Kolmogorov-Smirnov-Lilliefors tests to assess the conformity of the distributions of individual results and of laboratory means to normal distributions;
- Nalimov test to detect "outlying" values in the population of individual results and in the population of laboratory means;

- Bartlett test to assess the overall consistency of the variance values obtained in the participating laboratories;
- Cochran test to detect "outlying" values in the laboratory variances (s_i^2).

A summary of the statistical data, as obtained from computing, is given in Tables 16 –18.

Table 16 - Summary of statistical data for trace elements in BCR-713

Element	*As*	*Cd*	*Cr*	*Cu*	*Fe*
Number of accepted sets	11	17	14	16	13
Number of accepted replicates	64	102	84	96	78
Outlying variance (Cochran test)	No	0.70899, 0.55045	No	5.69421, 4.70124*	31.78679
Homogeneity of variances (Bartlett test)	No	No	No	No	No
Outlying mean values (Nalimov test)	No	No	No	No	No
Mean of means	9.66600	5.08820	21.93631	68.38219	398.30030
S_W	0.55490	0.29887	0.69231	2.64678	13.43779
S_B	0.77825	0.41580	1.77043	4.33220	23.89806
SD of distribution ofmeans	0.82342	0.43333	1.79285	4.46493	24.51964
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	About	Yes
0.95 % CI of the mean	0.55318	0.22280	1.03516	2.37918	14.81708
Element	*Mn*	*Ni*	*Pb*	*Se*	*Zn*
Number of accepted sets	16	11	16	10	11
Number of accepted replicates	96	66	96	60	66
Outlying variance (Cochran test)	No	No	4.48322, 3.09785*, 2.59985*	1.37650, 0.69272*	15.89365
Homogeneity of variances (Bartlett test)	No	No	No	No	No
Outlying mean values (Nalimov test)	No	No	No	No	No
Mean of means	43.39656	29.99500	46.52229	5.58058	199.96710
S_W	1.20095	1.20171	1.83077	0.54985	7.12061
S_B	2.25193	1.23603	2.59041	0.57086	24.77113
SD of distribution of means	2.30468	1.32983	2.69608	0.61340	24.94112
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	Yes	About
0.95 % CI of the mean	1.22807	0.89340	1.43663	0.43881	16.75577

*It is a straggler

Table 17 - Summary of statistical data for trace elements in BCR-714

Element	*As*	*Cd*	*Cr*	*Cu*	*Fe*
Number of accepted sets	12	16	15	15	14
Number of accepted replicates	72	96	90	90	84
Outlying variance (Cochran test)	2.16025, 1.91547*	No	4.74739*	No	74.14763, 42.62237*
Homogeneity of variances (Bartlett test)	No	No	No	No	No
Outlying mean values (Nalimov test)	No	No	No	No	No
Mean of means	18.32868	19.92917	122.97020	309.07010	1029.95800
S_W	0.94898	0.69992	2.32870	8.92015	28.97601

Element	*As*	*Cd*	*Cr*	*Cu*	*Fe*
S_B	1.48395	0.85043	4.69930	13.53598	45.83587
SD of distribution ofmeans	1.53369	0.89715	4.79450	14.01729	47.33773
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	Yes	Yes
0.95 % CI of the mean	0.97446	0.47805	2.65510	7.76248	27.33197
Element	*Mn*	*Ni*	*Pb*	*Se*	*Zn*
Number of accepted sets	16	14	19	9	14
Number of accepted replicates	96	84	113	54	84
Outlying variance (Cochran test)	No	No	13.67358, 10.71173	1.08934*	87.00498, 67.39323
Homogeneity of variances (Bartlett test)	No	No	No	No	No
Outlying mean values (Nalimov test)	No	No	No No	No	No
Mean of means	103.10910	107.51640	144.88760	9.76268	1023.09900
S_W	2.68537	1.97129	5.57829	0.57596	33.70388
S_B	4.28738	3.42419	8.05226	0.67456	58.4377
SD of distribution of means	4.42532	3.42419	8.33423	0.71437	60.03581
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	Yes	Yes
0.95 % CI of the mean	2.35808	2.03094	4.01694	0.54911	34.66364

*It is a straggler

Table 18 - Summary of statistical data for trace elements in BCR-715

Element	*As*	*Cd*	*Cr*	*Cu*	*Fe*
Number of accepted sets	10	17	15	14	13
Number of accepted replicates	60	102	89	84	78
Outlying variance (Cochran test)	No	4.01497, 3.62080, 2.17226*	50.14280	No	146.34430, 101.71070*
Homogeneity of variances (Bartlett test)	Yes	No	No	No	No
Outlying mean values (Nalimov test)	No	No	No	No	No No
Mean of means	28.64017	40.41000	997.59630	895.34310	3015.86600
S_W	0.81446	1.63017	21.00138	24.09338	62.26873
S_B	1.96475	1.63506	45.71806	28.68137	160.42380
SD of distribution ofmeans	1.99268	1.76532	46.35258	30.32109	162.42540
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	Yes	Yes
0.95 % CI of the mean	1.42549	0.90764	25.66913	17.50684	98.15283
Element	*Mn*	*Ni*	*Pb*	*Se*	*Zn*
Number of accepted sets	15	11	18	8	15
Number of accepted replicates	90	64	107	48	90
Outlying variance (Cochran test)	17.67038, 12.13316	50.41296	40.88313, 31.74902, 29.02163	No	276.48290
Homogeneity of variances (Bartlett test)	No	No		Yes	No
Outlying mean values (Nalimov test)	No No	1103.33300	No No	No	No
Mean of means	248.06370	1201.38200	494.34030	28.05229	3999.19300

S_W	6.95022	22.55465	16.52032	0.75293	113.24550
S_B	12.75662	38.41759	18.59987	2.04960	118.18690
SD of distribution of means	13.06836	39.18124	19.70914	2.07253	126.90770
Data sets means normally distributed? (Kolmogorov-Smirnov-Lilliefors test)	Yes	Yes	Yes	Yes	Yes
0.95 % CI of the mean	7.23700	26.32251	9.80106	1.73269	70.27905

*It is a straggler

Pertinent information derived from the normality test and Nalimov test applied to laboratory means populations are reported in section 8.3 as well as the outcome of Cochran and Bartlett´s tests on the laboratory variances.

For Cochran and Nalimov test, a value is called an "outlier" when the hypothesis that it belongs to the population of results considered can be rejected with a 0.01 risk error. The criterion was adopted that an "outlier" of variance would be eliminated only if the standard error of the mean ($s_i/\sqrt{n_i}$) of the set exceed the standard deviation of the distribution of all laboratory means.

The sets of results found acceptable on technical and statistical grounds are represented in the form of "bar- Charts" in Annex I. In the figures the length of a bar corresponds to the 95 % confidence interval of the mean. The certified values were calculated as the arithmetic means of laboratory means (taking into account the number of sets accepted for certification after both statistical and technical scrutiny); they are featured as vertical dotted lines on the bar-graphs.

7.2 Statistical evaluation of the results

The purpose of this examination is essential to ensure that the population of results accepted for certification has a normal distribution before the mean values and the 95 % confidence interval of the means of means are calculated. This was true in all cases (Kolmogorov-Smirnov-Lilliefors tests), except for Cu and Zn in BCR-713 that are about the normal.

The estimate of the within-laboratory standard deviation (S_W) and the between-laboratory standard deviation (S_B), as derived from one way analysis of variance, demonstrate that the between-laboratory variation was the major source of variability between results. The set of variances is often not homogeneous which is due to the fact that different analytical methods are used each having a different repeatibility and reproducibility. If one single method was used then a homogeneous set of laboratory variances would be required. It is also for that reason that the S_W calculated is purely indicative and not really applicable to any particular method because it is a composite value for all the methods used in the particular certification. For reason of uniformity, it was decided to base the certification on the laboratory means rather than on all individual results.

Table 19 Laboratories with outlying or straggling variances

Element	*BCR-713*	*BCR-714*	*BCR-715*
As		Lab 17 (outlier), Lab 06 (straggler)	
Cd	Lab 08 and Lab 15 (outlier)		Lab 16 and Lab 15 (outlier), Lab 12 (straggler)
Cr		Lab 11 (straggler)	Lab 16 (outlier)
Cu	Lab 01 (outlier), Lab 11 (straggler)		
Fe	Lab 15 (outlier)	Lab 06 (outlier), Lab 11 (straggler)	Lab 11 and Lab 12 (outliers)
Mn			Lab 11 and Lab 16 (outliers)
Ni			Lab 10 (outlier)
Pb	Lab 13 (outlier), Lab 06 and Lab 16 (stragglers)	Lab 06 and Lab 12 (outliers)	Lab 06, Lab 16 and Lab 12 (outliers).
Se	Lab 10 (outlier), Lab 16 (straggler)	Lab 10 (straggler)	
Zn	Lab 06 (outlier)	Lab 02 and Lab 10 (outlier)	Lab 10 (outlier)

All these data were kept since they satisfied the criterion of acceptance (Section 8.2).

8. CERTIFIED VALUES AND UNCERTAINTIES

The evaluation of uncertainties in the context of certification exercises has evolved over the past decade. Nowadays, certified values should be accompanied by uncertainty statements in compliance with the requirements made by GUM [10]. While the design of new certification projects consider the needs for a proper estimation of the various uncertainty sources such as stability and homogeneity, older campaigns aimed only on qualitative statements (yes/no decisions) whether a material was stable and homogeneous.

The evaluation described hereafter is based on a concept described by Pauwels *et al.* [11 and literature cited] and uses available data discussed in the previous chapters.

8.1.1 Conceptual considerations

Based on the findings obtained in the stability and homogeneity studies as well as the scattering of results in the batch characterisation estimates for u_{bb} (homogeneity), u_{lts} (long-term-stability) and u_{char} (batch characterisation) were obtained and combined according the following equation:

$$U_{CRM} = 2 \cdot \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

Due to the transport conditions selected for dispatch, the uncertainty constituent for short-term stabililty (u_{sts}) is negligible and consequently not included in the overall uncertainty. The estimation of the other uncertainty sources is described below.

8.1.2 Uncertainty source "homogeneity"

The homogeneity study is described in chapter 4. From these data, an estimation of u_{bb} was derived from the homogeneity study as described by Linsinger *et al.* [12].

According to this approach, s_{bb} (being the standard deviation between units) or u^*_{bb} (being the upper limit of inhomogeneity that can be hidden by the method repeatability) are used as estimates of u_{bb}. Values for s_{bb} and u^*_{bb} were calculated accordingly:

Whereas estimates for s_{bb} were estimated from the differences of the observed $(CV_{bb})^2$ and $(CV_{ib})^2$ as shown in Table 3, values for u^*_{bb} were calculated as:

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MSwithin}}},$$

where n is the number of replicates per unit and $\nu_{MSwithin}$ the degrees of freedom of MS_{within};

If the value of s_{bb} is below the minimum value as determined by the repeatability of the method and the number of replicates performed, u^*_{bb} is used to estimate u_{bb}. The results of these calculations are shown in Table 20.

8.1.3 Uncertainty source "stability"

Similarly, a quantitative estimate of the uncertainty related to stability, u_{lts}, was obtained plotting the shelf-life as described elsewhere [12]. The uncertainty was estimated for a shelf-life of 12 months only, as the data were insufficient to allow a further projection without seriously compromising the usefulness of the certified values. Thus, the estimated uncertainty

contribution, u_{lts}, can be used to establish expiry dates once appropriate stability testing data are available, e.g. after having performed an isochronous experiment.

8.1.4 Uncertainty source "batch characterisation"

An estimate for u_{char} was derived from the standard error obtained on the mean of laboratories means.

8.1.5 Uncertainty budget

Based on these uncertainty contributions the following uncertainty budget is established:

Table 20 - Uncertainty budget for BCR-713, -714 and –715. Concentrations are in µg/L.

Material	*Parameter*	*Mean value*	u_{char} *(%)*	s_{bb} *(%), n=20*	u^*_{bb} *(%), df=9*	u_{lts} *(%), 12 months*	U_{CRM} *(%)*	U_{CRM}
BCR-713	As	9.66	2.57	2.71	2.88	3.55	10.49	1.01
	Cd	5.09	2.06	*/*	3.43	3.64	10.82	0.55
	Cr	21.94	2.18	0.96	1.51	4.67	10.74	2.36
	Cu	68.38	1.63	0	0.89	1.53	4.81	3.29
	Fe	398.3	1.71	*/*	2.54	2.6	8.03	32.00
	Mn	43.4	1.33	1.44	1.65	2.62	6.74	2.93
	Ni	30.36	1.74	2.29	3.43	6.61	15.30	4.64
	Pb	46.52	1.45	1.3	1.3	2.59	6.48	3.01
	Se	5.58	3.48	*/*	4.8	6.62	17.77	0.99
	Zn	216.16	5.86	*/*	2.4	3.89	14.86	32.13
BCR-714	As	18.33	2.42	*/*	1.44	3.35	8.75	1.60
	Cd	19.93	1.13	*/*	1.03	3.51	7.66	1.53
	Cr	122.97	1.01	0	1.1	3.73	8.04	9.88
	Cu	309.07	1.17	*/*	0.89	3.31	7.24	22.39
	Fe	1029.96	1.23	2.13	1.99	4.36	10.01	103.12
	Mn	103.11	1.07	0.92	1.37	4.43	9.52	9.81
	Ni	108.48	1.2	*/*	2.06	6.28	13.43	14.57
	Pb	144.89	1.32	*/*	1.99	2.5	6.91	10.02
	Se	9.76	2.44	1	3.43	4.04	11.67	1.14
	Zn	1023.1	1.57	0	0.96	4.28	9.32	95.33
BCR-715	As	28.64	2.2	1.53	1.44	4.55	10.56	3.02
	Cd	40.41	1.06	0.75	0.89	5.09	10.55	4.26
	Cr	997.6	1.2	0.56	1.03	4.14	8.86	88.42
	Cu	895.34	0.91	*/*	0.82	7.23	14.67	131.31
	Fe	2995.21	1.4	1.55	1.17	3.86	8.78	262.91
	Mn	248.06	1.36	*/*	1.51	4.5	9.88	24.50
	Ni	1206.89	1.03	*/*	0.69	3.09	6.66	80.37
	Pb	494.06	0.94	*/*	1.1	2.93	6.54	32.29
	Se	28.77	3.35	*/*	1.85	5.53	13.45	3.87
	Zn	3999.19	0.82	*/*	0.89	4.7	9.71	388.19

8.2 Certified values

The certified values and their associated uncertainties are given in the tables below. Expanded uncertainties (coverage factor k=2) were expressed according to the Guide for the Expression of Uncertainties in Measurement (GUM).

Table 21 – Certified values and Uncertainties. All concentrations are expressed in µg/L.

Elements	*BCR-713*	*BCR-714*	*BCR-715*
As	9.7 ± 1.1	18.3 ± 1.6	29 ± 4
Cd	5.1 ± 0.6	19.9 ± 1.6	40 ± 5
Cr	21.9 ± 2.4	123 ± 10	$(1.00 \pm 0.09) \cdot 10^3$
Cu	69 ± 4	309 ± 23	$(0.90 \pm 0.14) \cdot 10^3$
Fe	$(0.40 \pm 0.04) \cdot 10^3$	$(1.03 \pm 0.11) \cdot 10^3$	$(3.00 \pm 0.27) \cdot 10^3$
Mn	43.4 ± 3.0	103 ± 10	248 ± 25
Ni	30 ± 5	108 ± 15	$(1.20 \pm 0.09) \cdot 10^3$
Pb	47 ± 4	145 ± 11	$(0.49 \pm 0.04) \cdot 10^3$
Se	5.6 ± 1.0	9.8 ± 1.2	29 ± 4
Zn	$(0.22 \pm 0.04) \cdot 10^3$	$(1.00 \pm 0.10) \cdot 10^3$	$(4.00 \pm 0.40) \cdot 10^3$

9. INSTRUCTIONS FOR USE

9.1 Instructions for handling of the sample

Each material contains 100 mL of a wastewater reference material in Pyrex ampoule. Before an ampoule is opened, it should be shaken manually so that the material within is re-homogenised. Personnel should wear non-powdered polythene gloves and dust free garments. Each ampoule contains HNO_3 so, handle with care.

9.2 Use of the certified values

These materials may be used to check the precision and the trueness of the laboratory measurement process according to ISO Guide 33 [13].

9.2.1 Assessment of precision

The precision of the measurement process is assessed by comparing the within-laboratory standard deviation determined during the certification step. All necessary equations are listed in detail in ISO Guide 33.

9.2.2 *Assessment of trueness*

The trueness of the measurement process is checked by comparing the average $\bar{x}$ of n measurement results with the certified value, μ. The criterion for acceptance of the results is as follows:

$$- a_2 - 2\,\sigma_D \leq \bar{x} - \mu \leq a_1 + 2\,\sigma_D$$

- a_1 and a_2 are adjustment values chosen by the experimenter according to economical or technical limitations or stipulations.
- $2\,\sigma_D$ is the long term within-laboratory standard deviation of the user's method.

However, if the reference material is used for confirming a calibration, the value to be used for each parameter is the certified mean value with the uncertainty at the 95 % confidence level.

10. REFERENCES

[1] European Council (1991). Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. *Official Journal* **L 135 (**30/05/1991), 40-52.

[2] Ph. Quevauviller, M. Valcarcel (1995). *The certification of the contents (amount of substance contents and mass fractions) of nitrate in simulated freshwater. Low content CRM 479. High content CRM 480.* European Commission EUR 16137 EN.

[3] Ph. Quevauviller, K. Andersen, J. Merry, H. van der Jagt (1998). *The certification of the contents (mass fractions) of aluminium, arsenic, cadmium, copper and lead in groundwater. Low content CRM 609. High content CRM 610.* European Commission EUR 18316 EN.

[4] Ph. Quevauviller, M. J. Beloliel, R. Neves Carneiro, L. Cortez (1998). *The certification of the contents (mass fractions) of calcium, chloride, magnesium, manganese, nitrate, phosphate, potassium, sodium and sulphate in artificial groundwater. High carbonate content CRM 616. Low carbonate content CRM 617.* European Commission EUR 18286 EN.

[5] Ph. Quevauviller, D. van Renterghem, B. Griepink, H. F. R. Reynders, H. van der Jagt (1993). *The certification of the contents (amount of substance contents) of ammonium, calcium, chloride, hydronium, magnesium, nitrate, potassium, sodium and sulphate in simulated rainwater. Low content CRM 408. High content CRM 409.* European Commission EUR 15024 EN.

[6] Ph. Quevauviller, K. J. M. Kramer, K. Vercoutere, B. Griepink (1992). *The certification of Cd, Cu, Pb, Mo, Ni and Zn in sea water. CRM 403.* European Commission EUR 14061 EN.

[7] Ph. Quevauviller, K. J. M. Kramer, T. Vinhas (1993). *The certification of the contents of Cd, Cu, Ni andZn in estuarine water. CRM 505.* European Commission EUR 16134 EN.

[8] Ph. Quevauviller, K. Andersen, J. Merry, H. van der Jagt (1998). *The certification of the contents (mass fractions) of bromide in groundwater based on ion chromatography measurements. Low content CRM 611. High content CRM 612.* European Commission EUR 18317 EN.

[9] M. Segura, Y. Madrid, C. Cámara, C. Rebollo, J. Azcárate, G. Kramer, Ph. Quevauviller (2000). *J. Environ. Monit.* **2**, 576-581.

[10] ISO-IEC-BIPM-IFCC-IUPAC-IUPAP-OIML. *Guide to the Expression of Uncertainties in Measurement (GUM),* Geneva, Switzerland (ISBN 92-67-10188-9).

[11] A.M.H. Van der Veen, T.P.J. Linsinger, H. Schimmel, A. Lamberty, J. Pauwels (2001). Uncertainty calculations in the certification of reference materials. 4. Characterisation and certification. *Accred. Qual. Assur.* **6**, 290-294.

[12] T.P.J Linsinger, J. Pauwels, A.M.H. van der Veen, H. Schimmel, A. Lamberty (2001). Homogeneity and stability of reference materials. *Accred. Qual. Assur.* **6**, 20-25.

[13] ISO Guide 33 (1989). *Uses of certified reference materials*. International Organization for Standardization, Geneva, Switzerland.

11. ANNEX I – INDIVIDUAL RESULTS

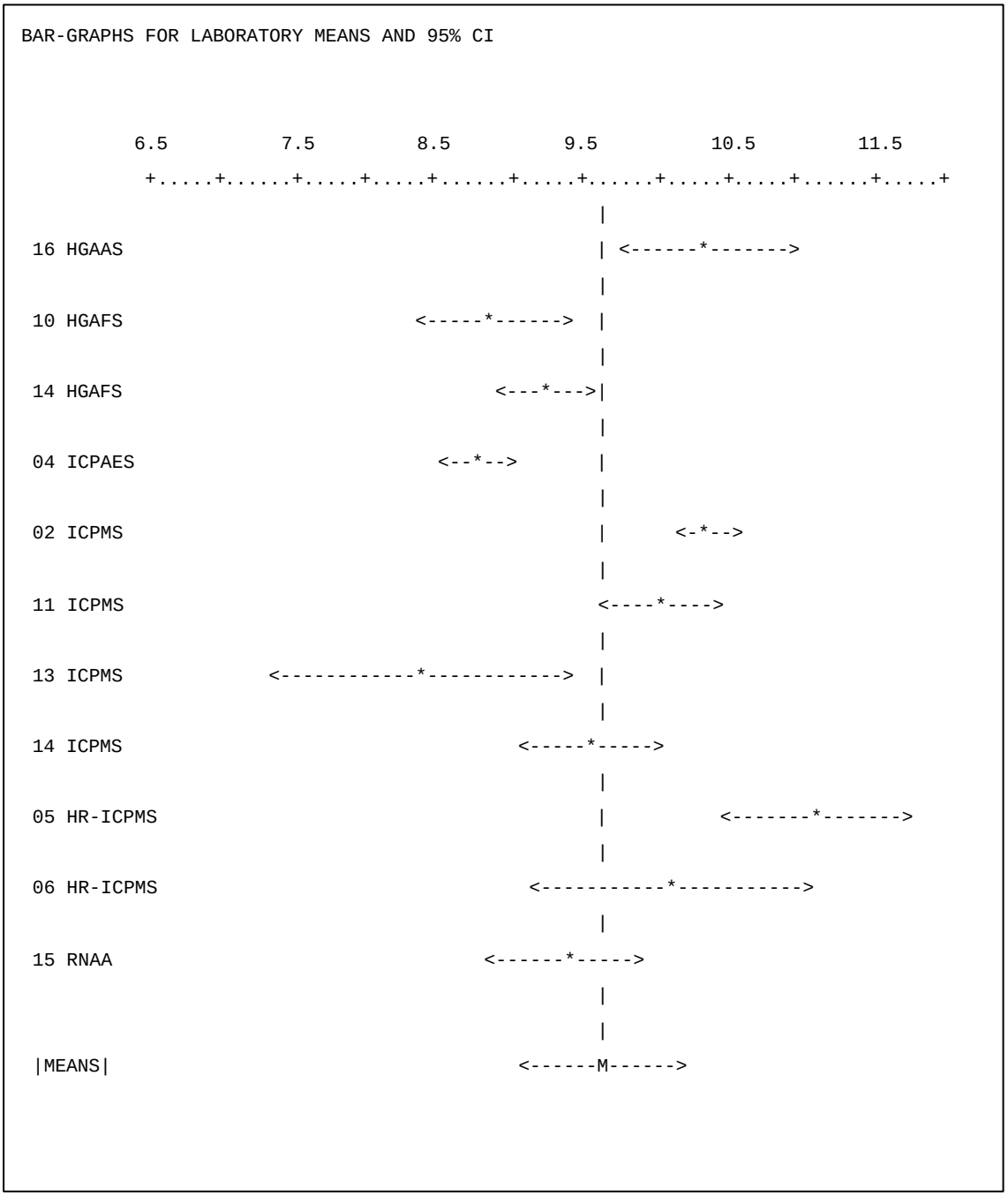

Figure 1 - Arsenic in BCR-713 in µg/L

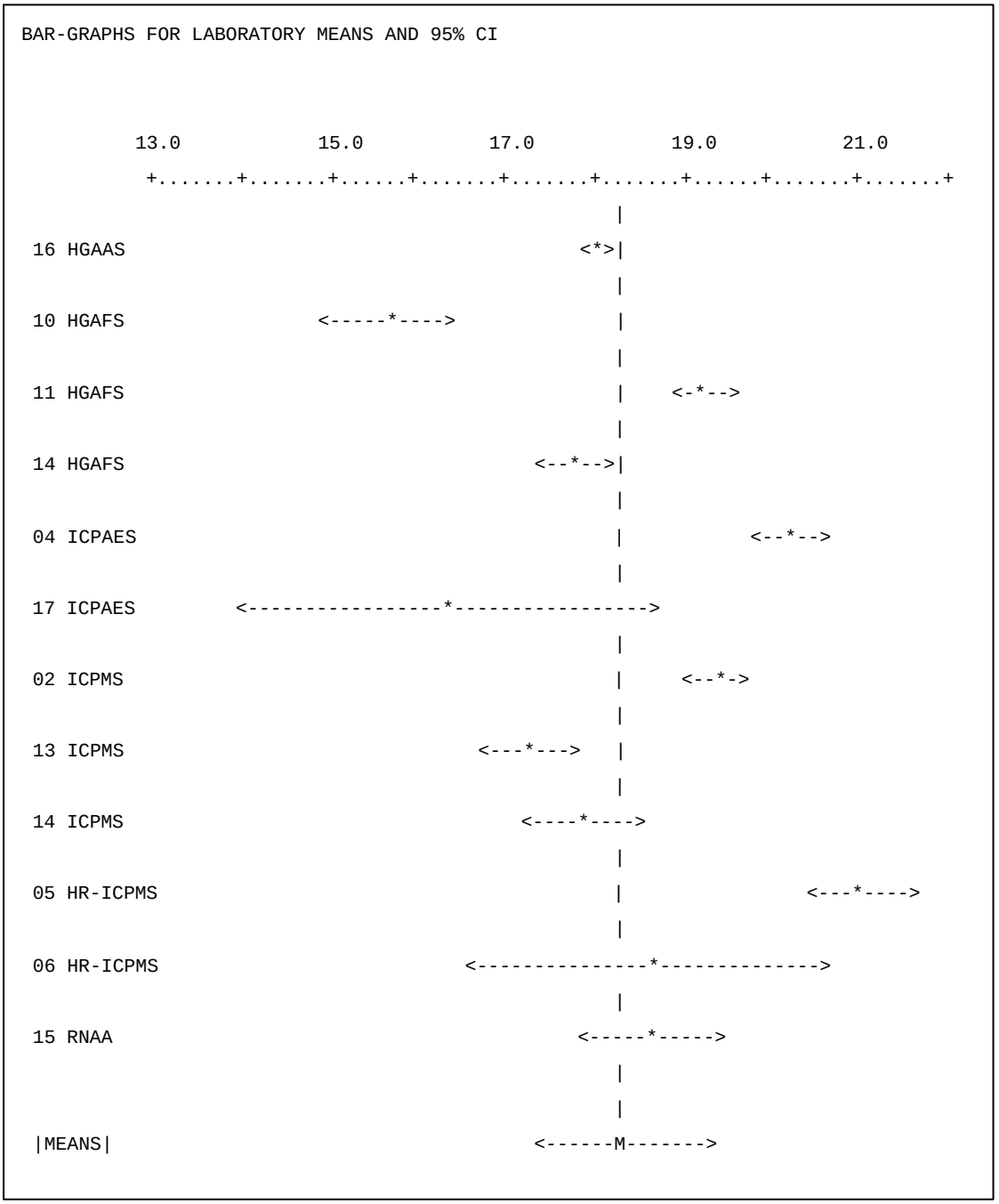

Figure 2 - Arsenic in BCR-714 in µg/L

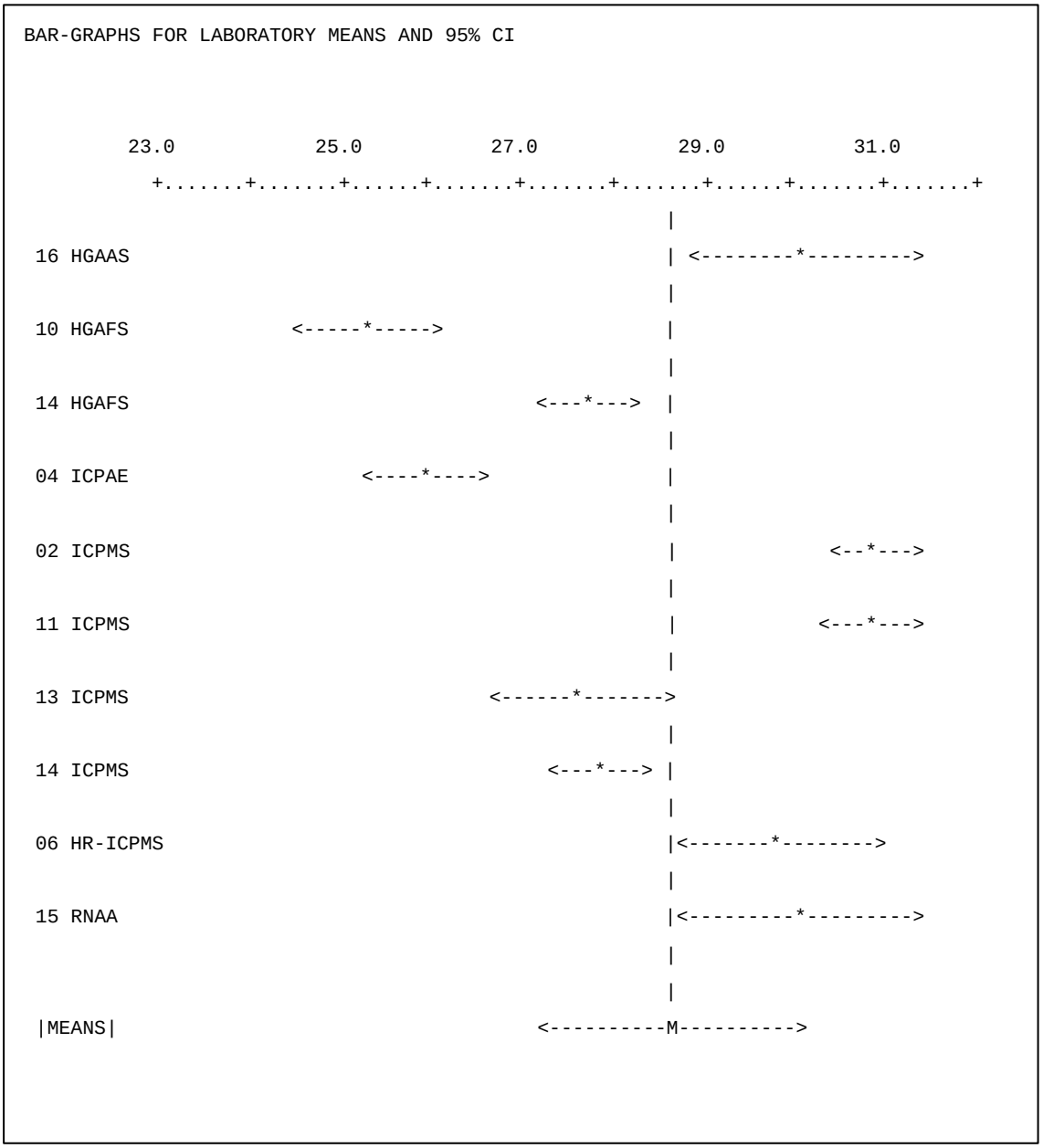

Figure 3 - Arsenic in BCR-715 in µg/L

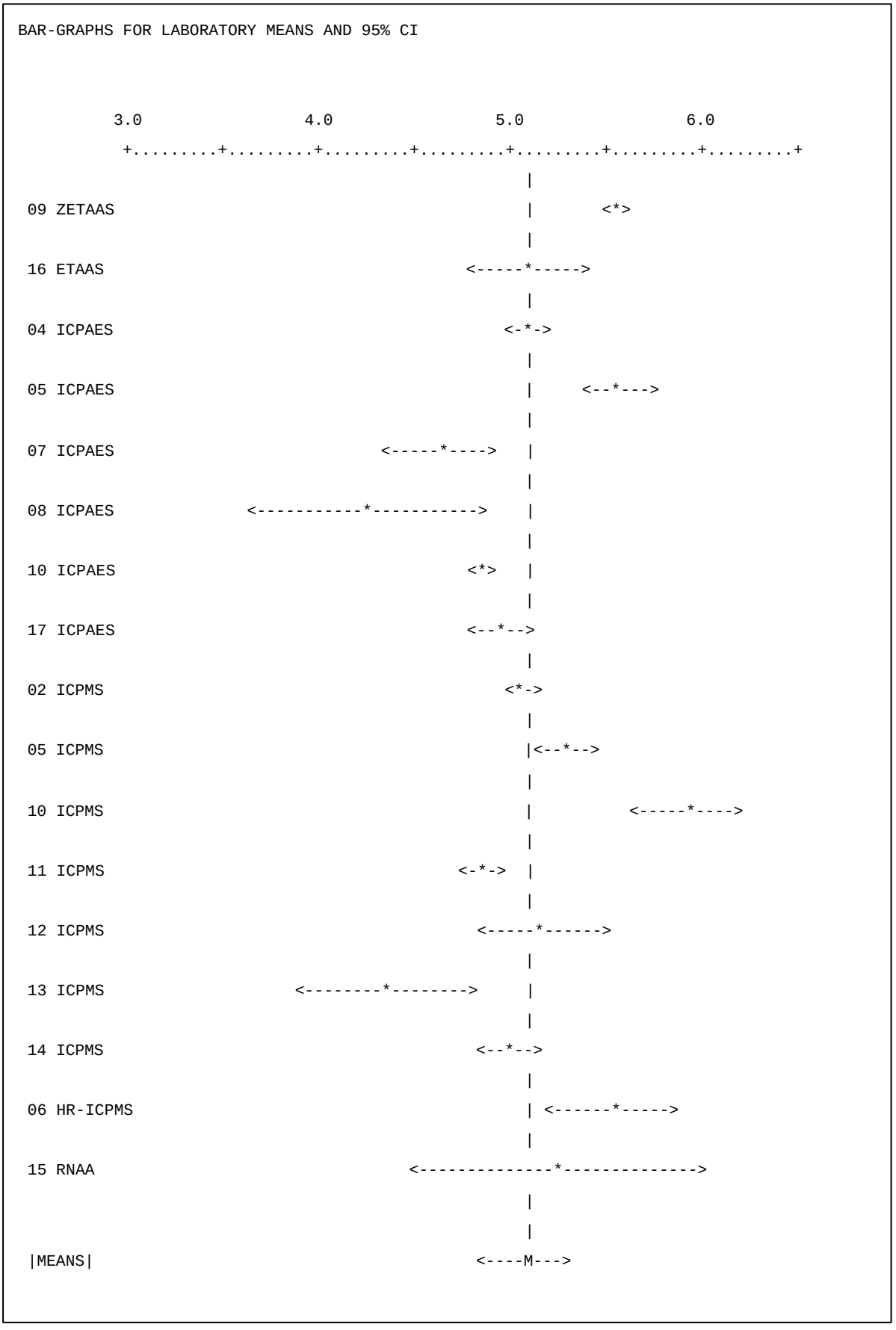

Figure 4 - Cadmium in BCR-713 in µg/L

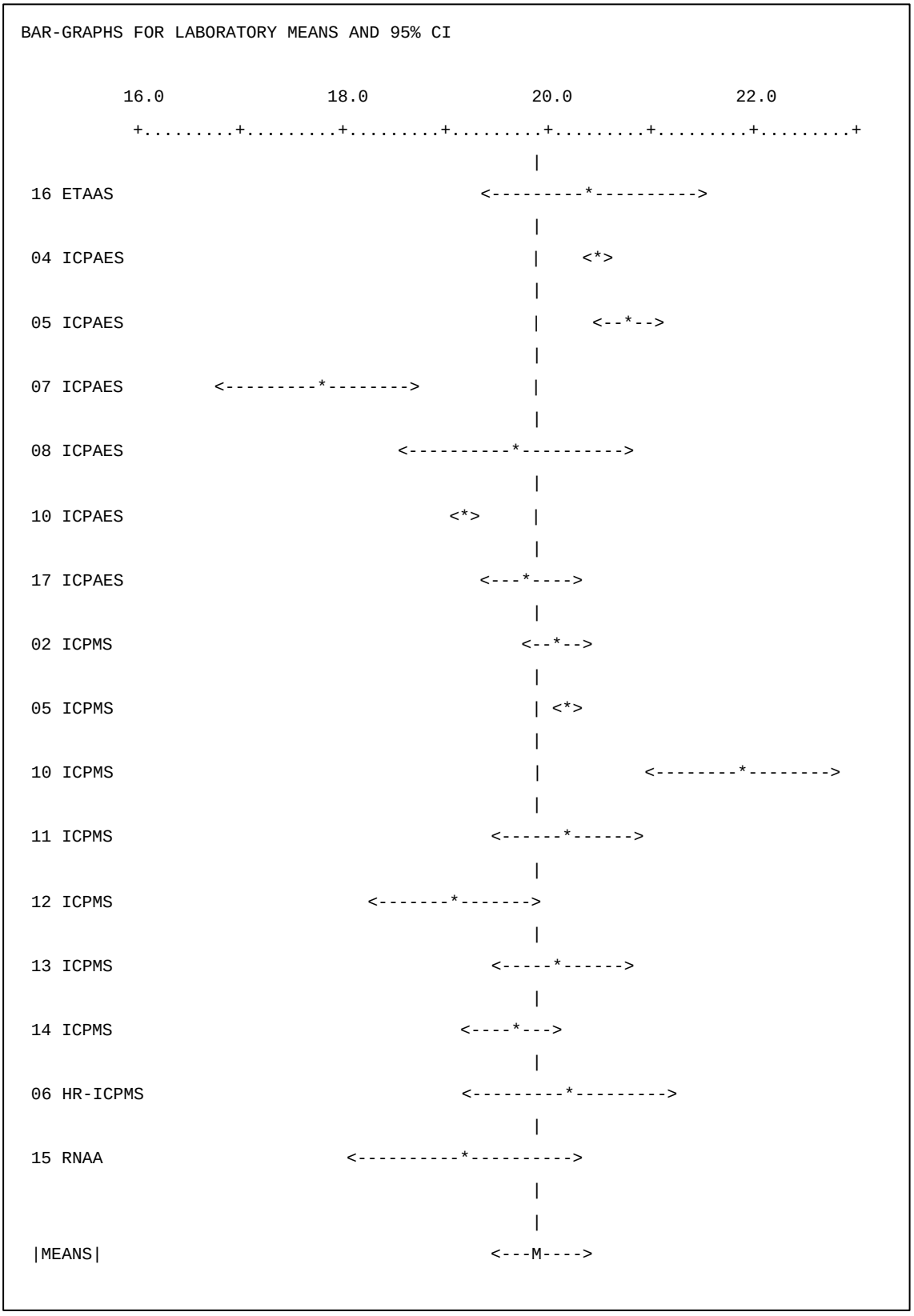

Figure 5 - Cadmium in BCR-714 in µg/L

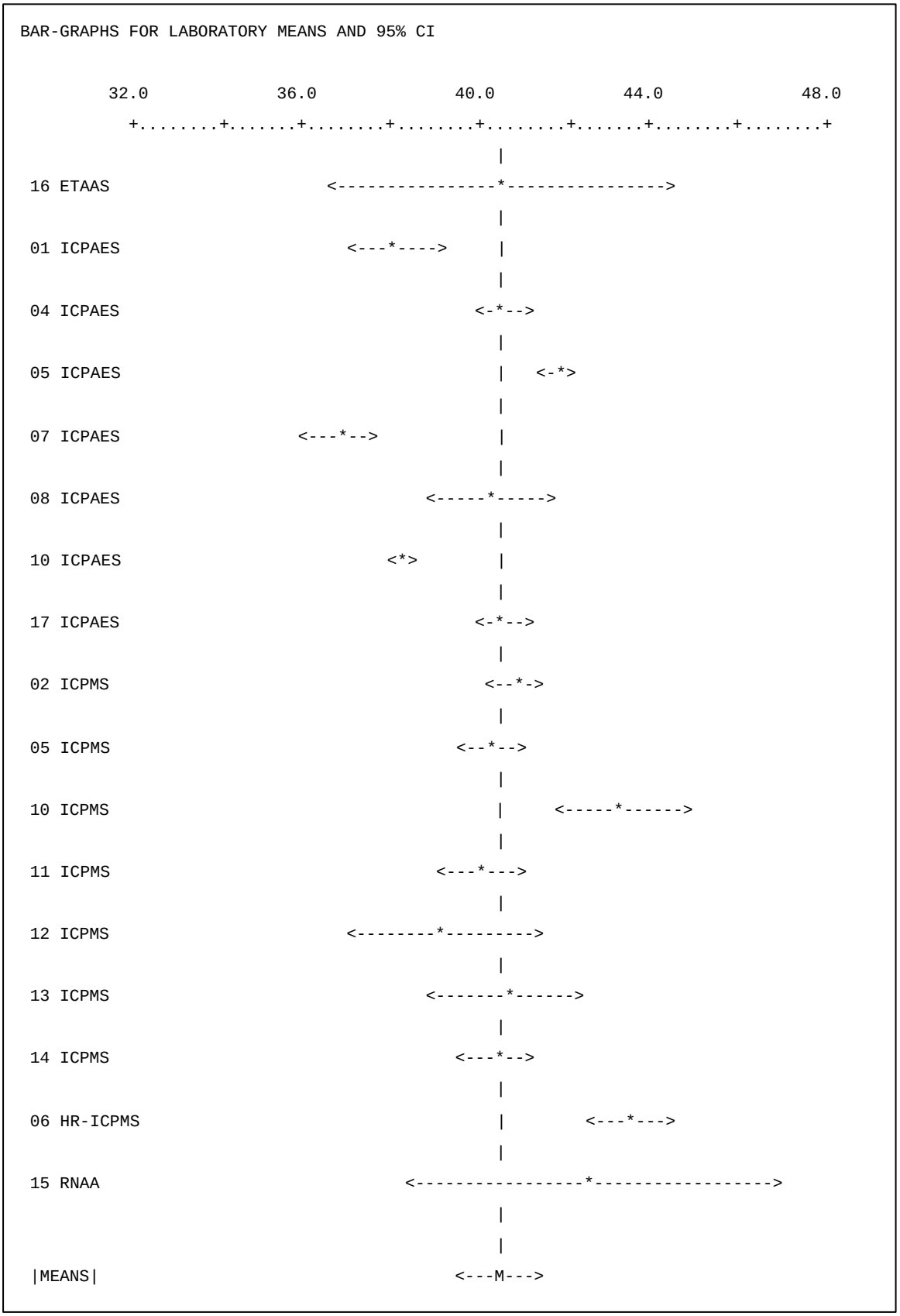

Figure 6 - Cadmium in BCR-715 in µg/L

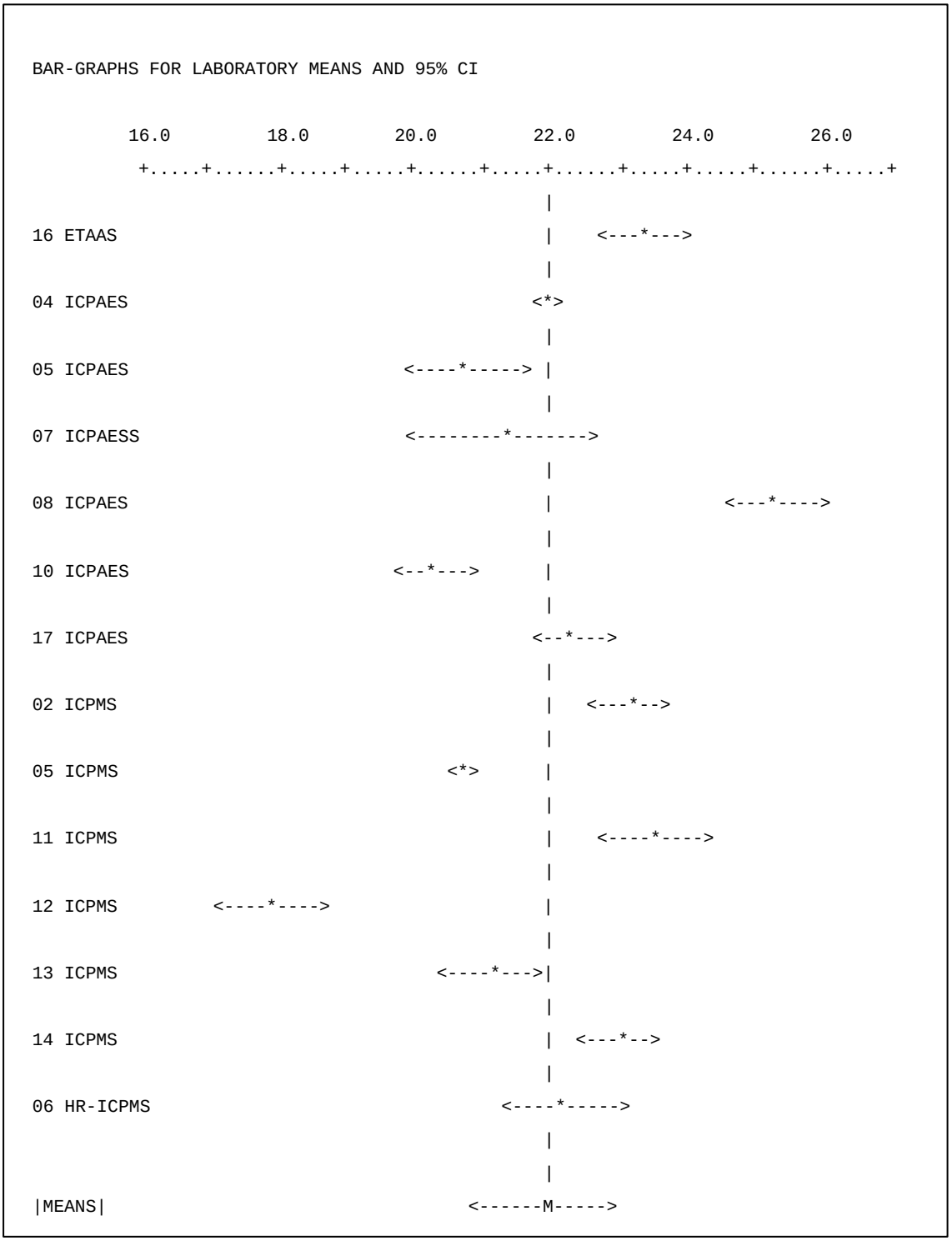

Figure 7 - Chromium in BCR-713 in µg/L

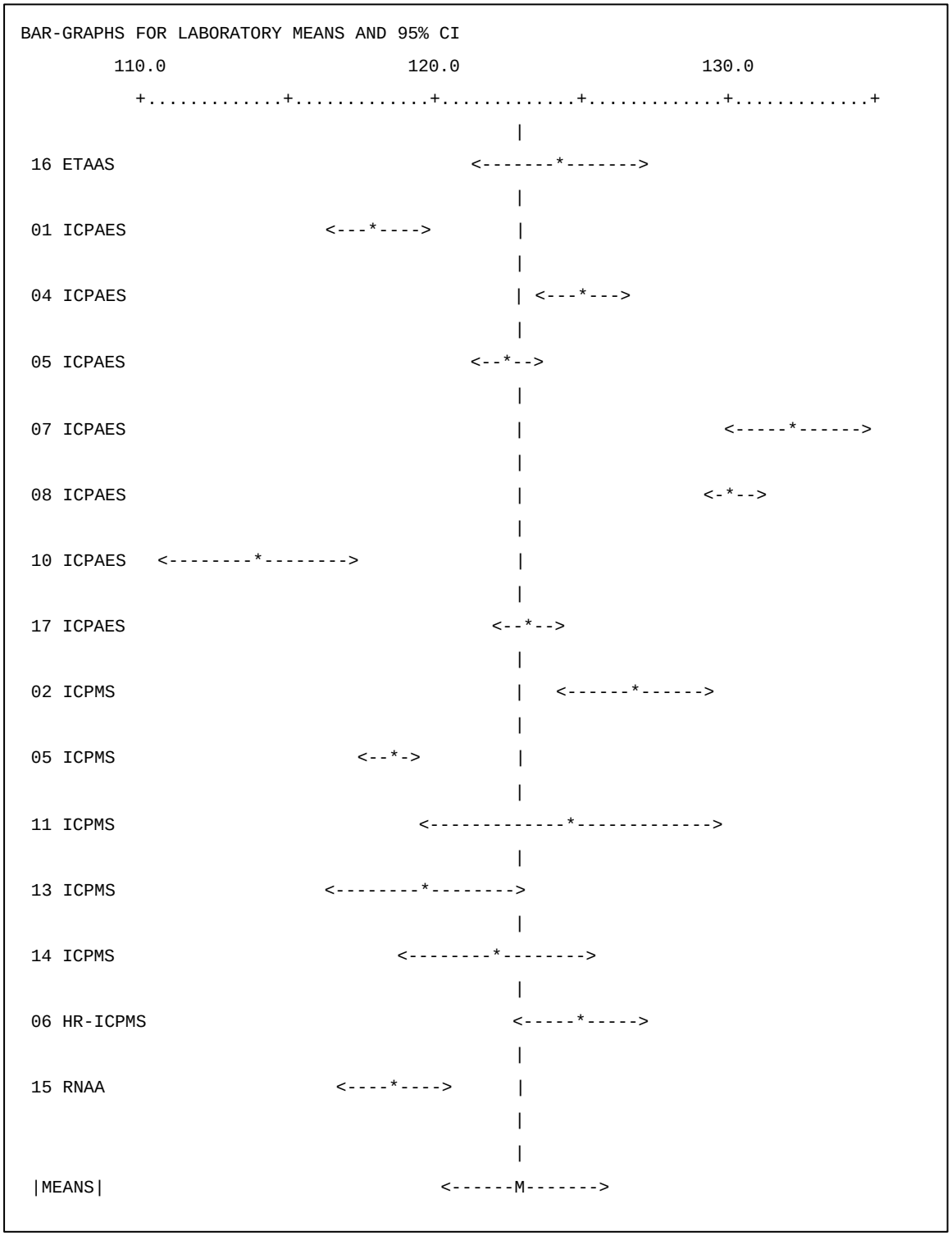

Figure 8 - Chromium in BCR-714 in µg/L

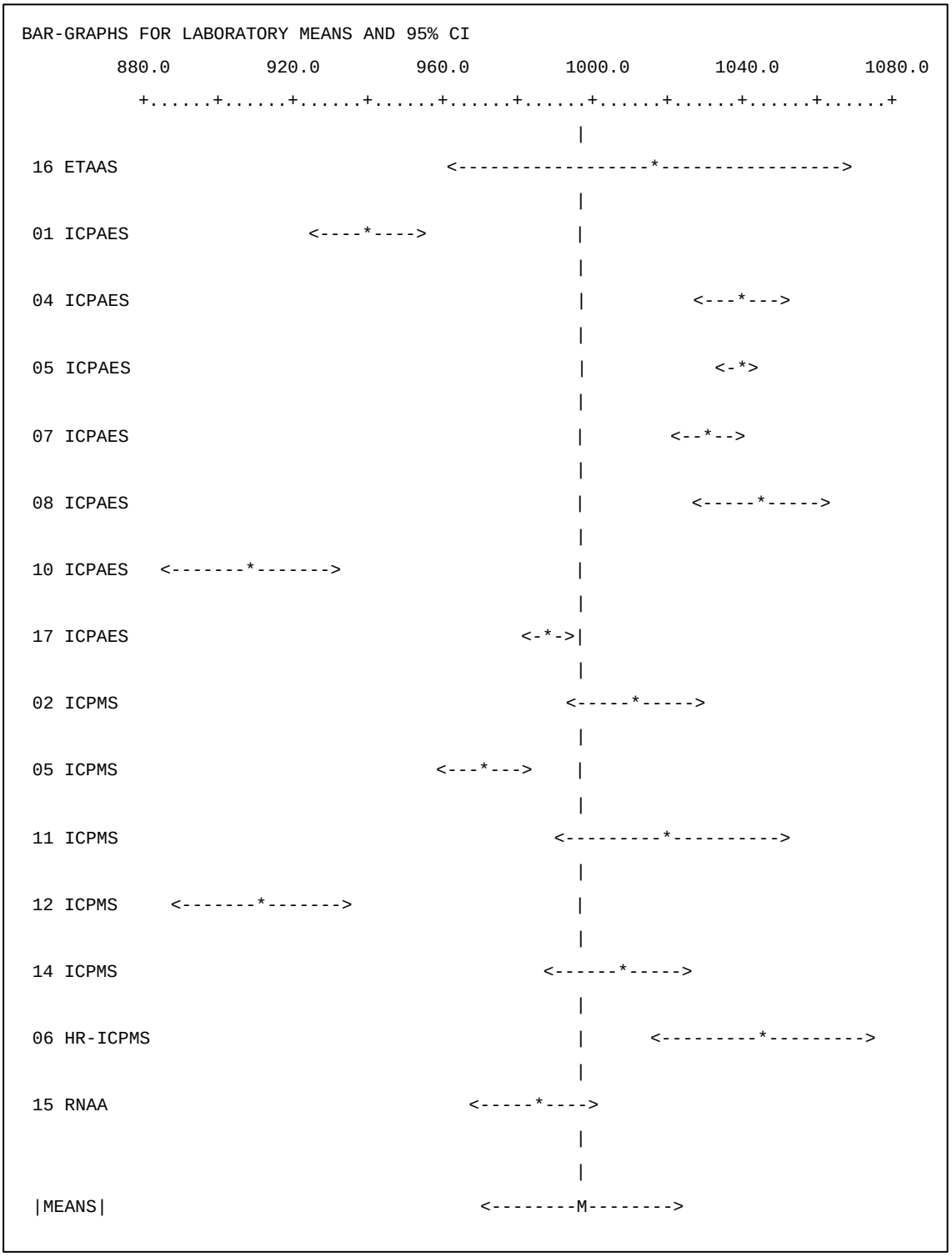

Figure 9 - Chromium in BCR-715 in µg/L

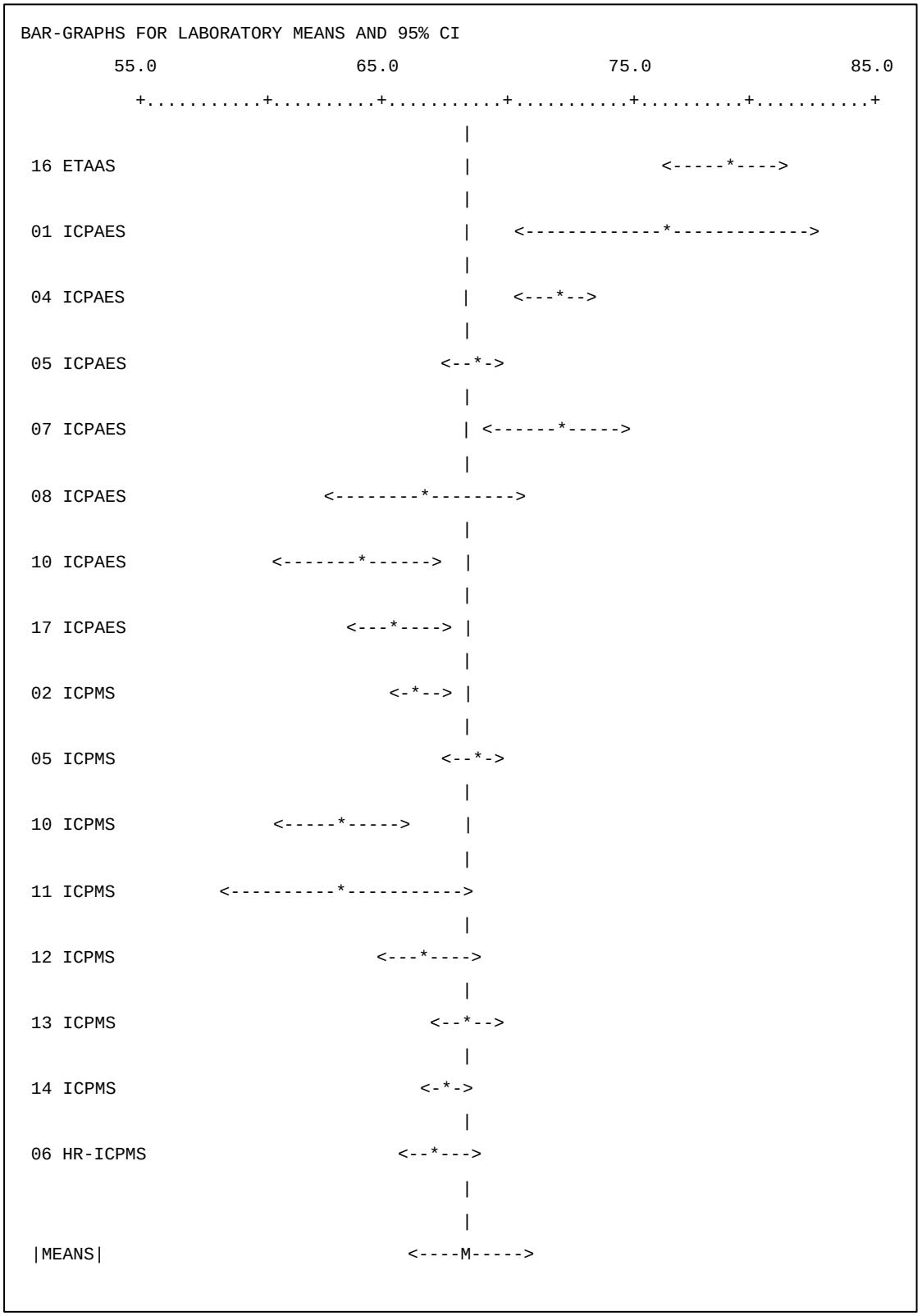

Figure 10 - Copper in BCR-713 in µg/L

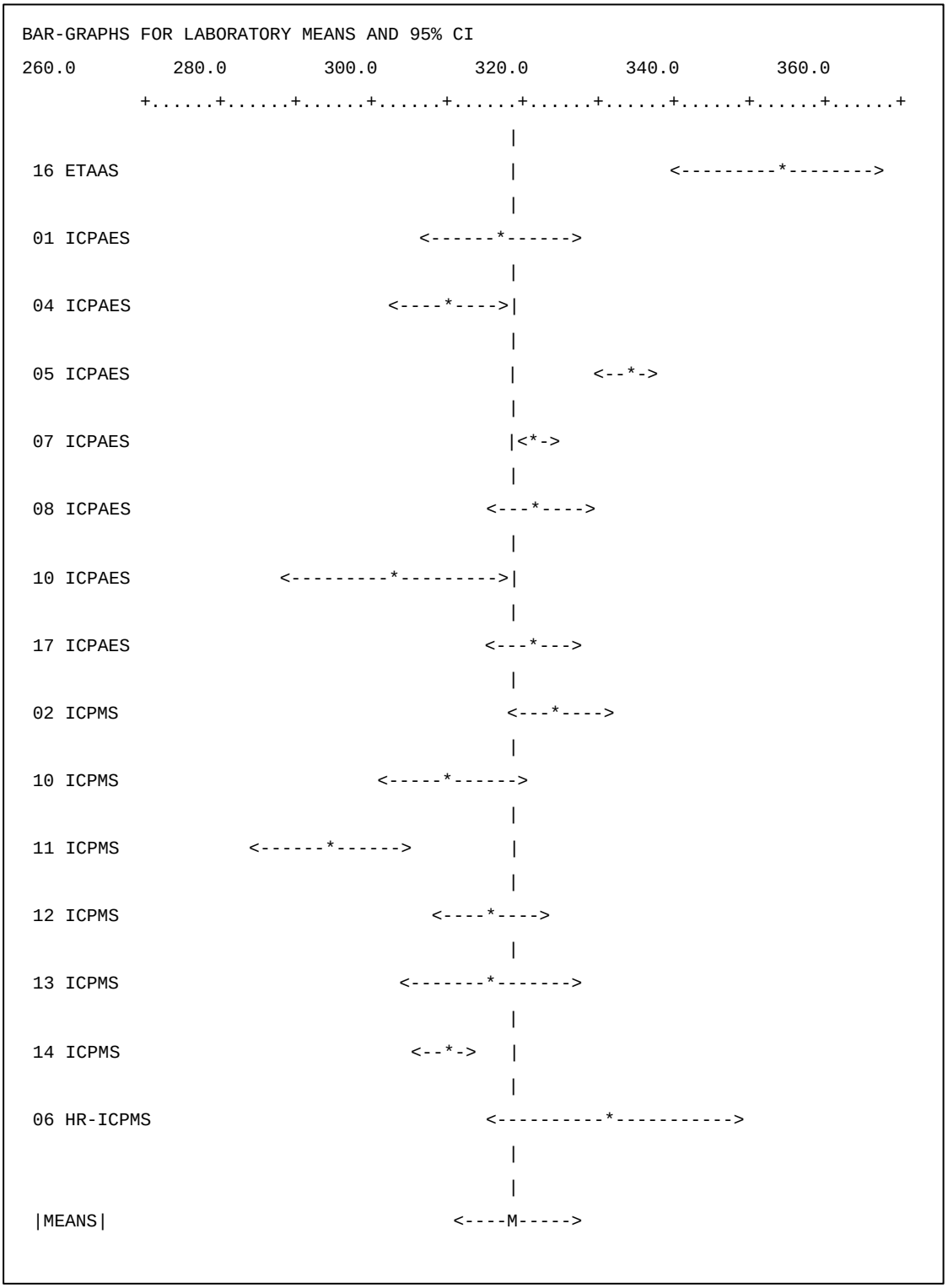

Figure 11 - Copper in BCR-714 in µg/L

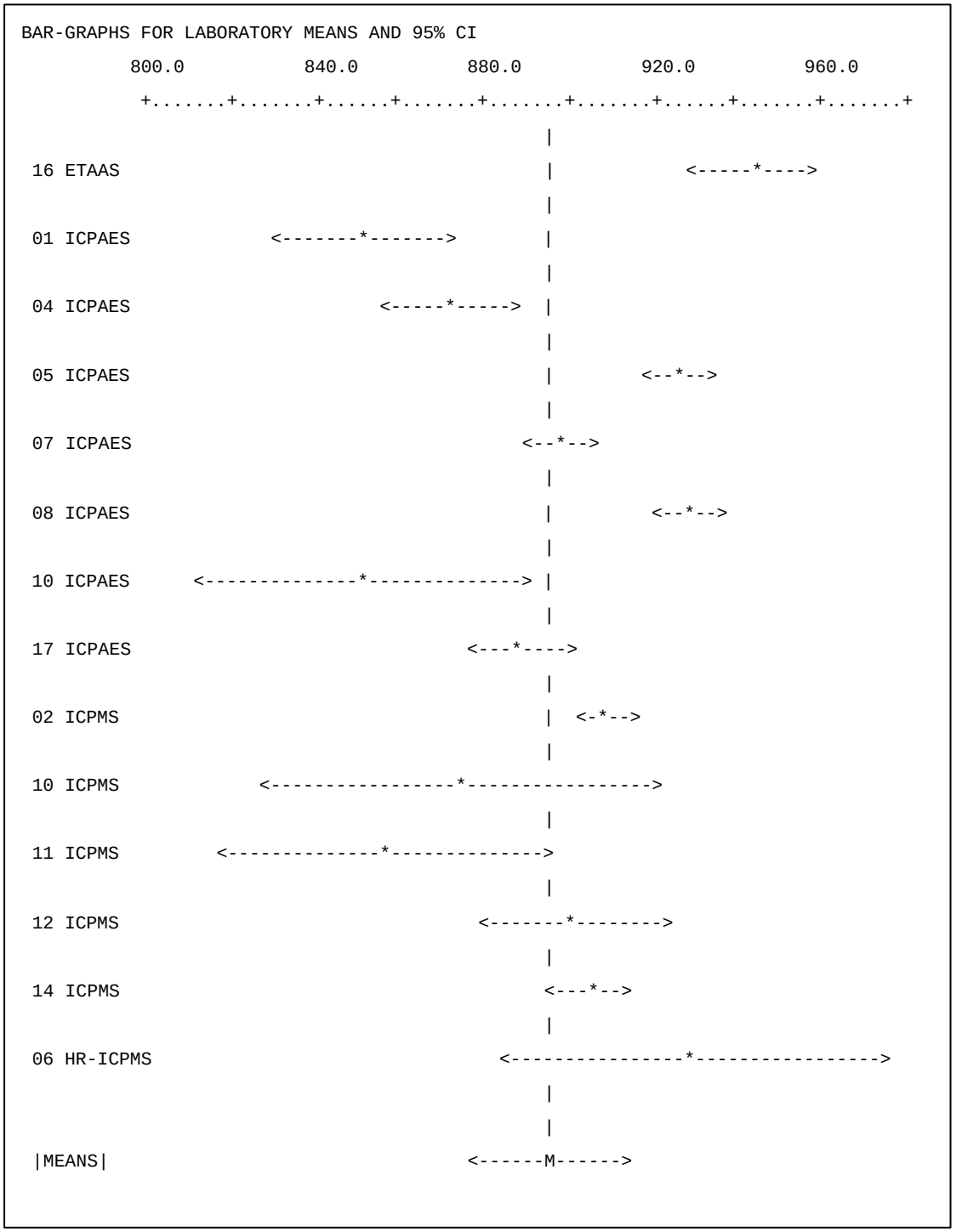

Figure 12 - Copper in BCR-715 in µg/L

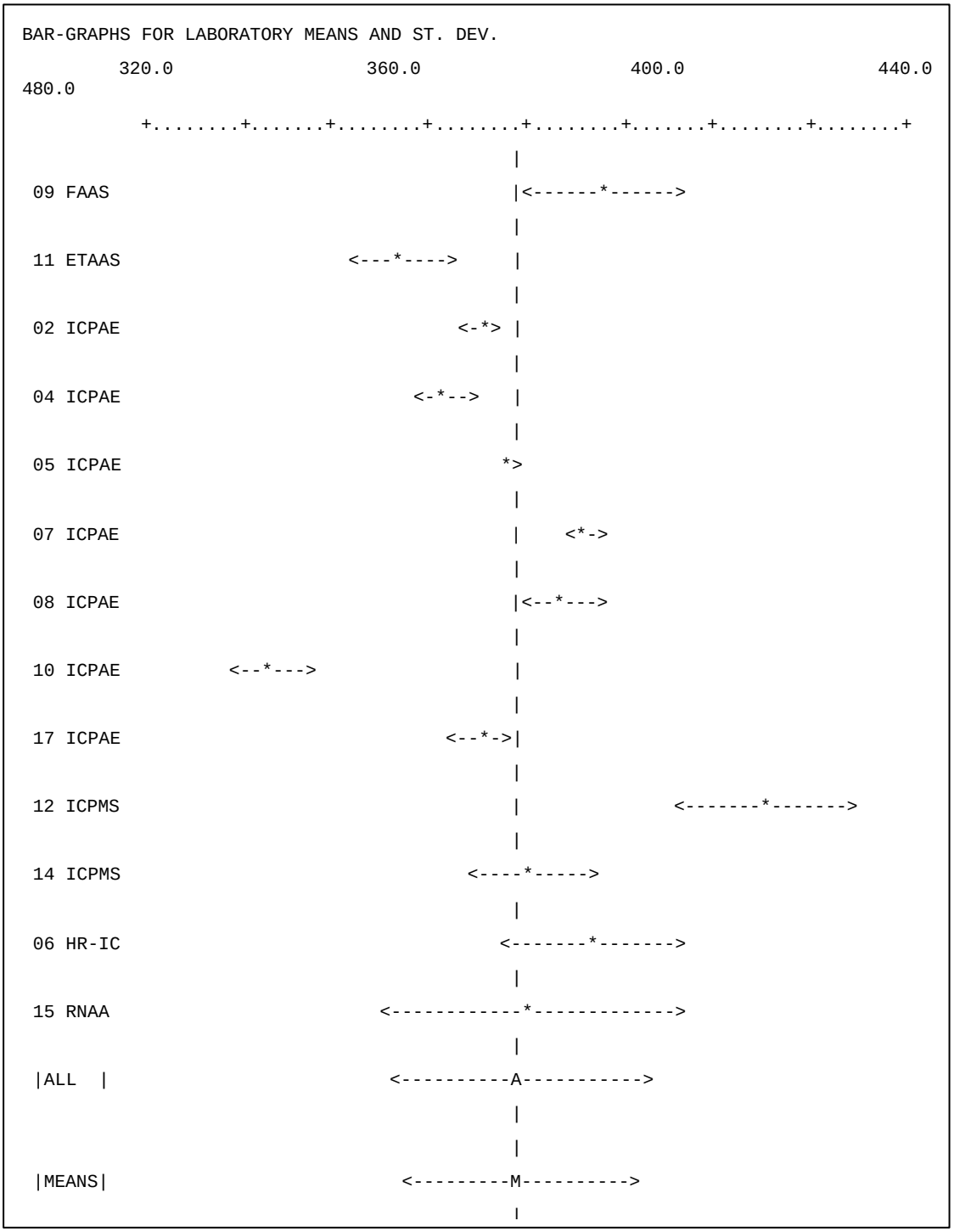

Figure 13 - Iron in BCR-713 in µg/L

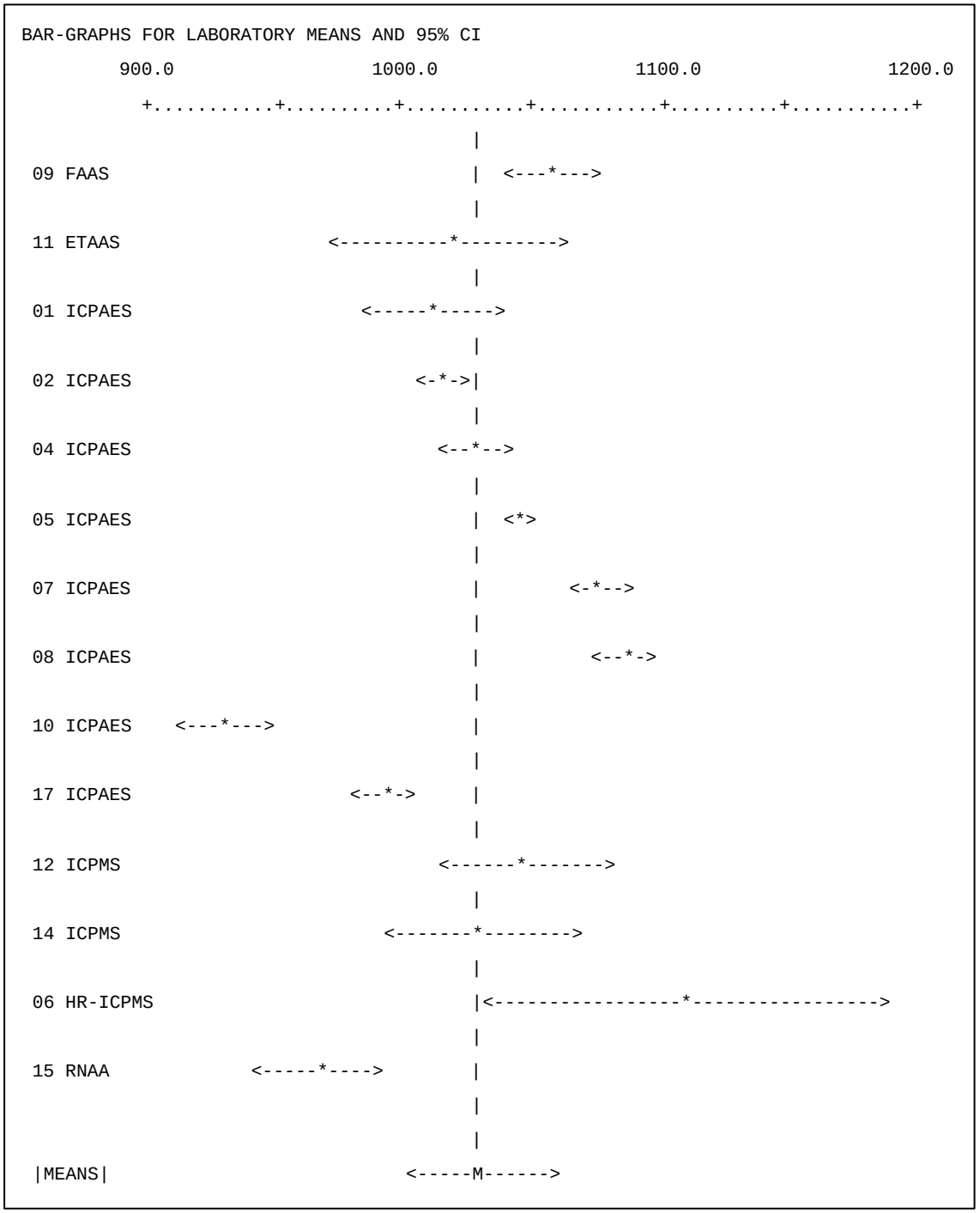

Figure 14 - Iron in BCR-714 in µg/L

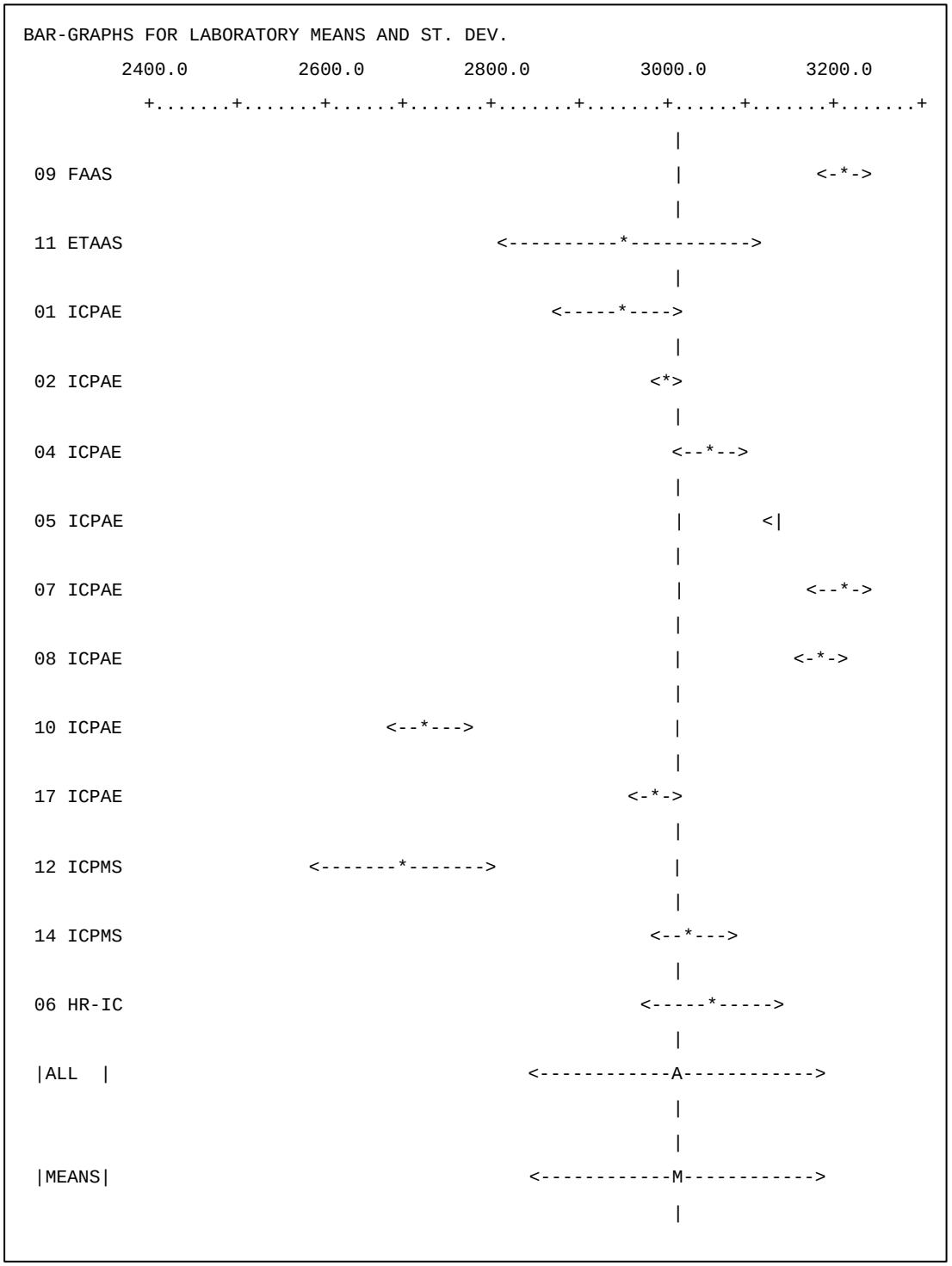

Figure 15 - Iron in BCR-715 in µg/L

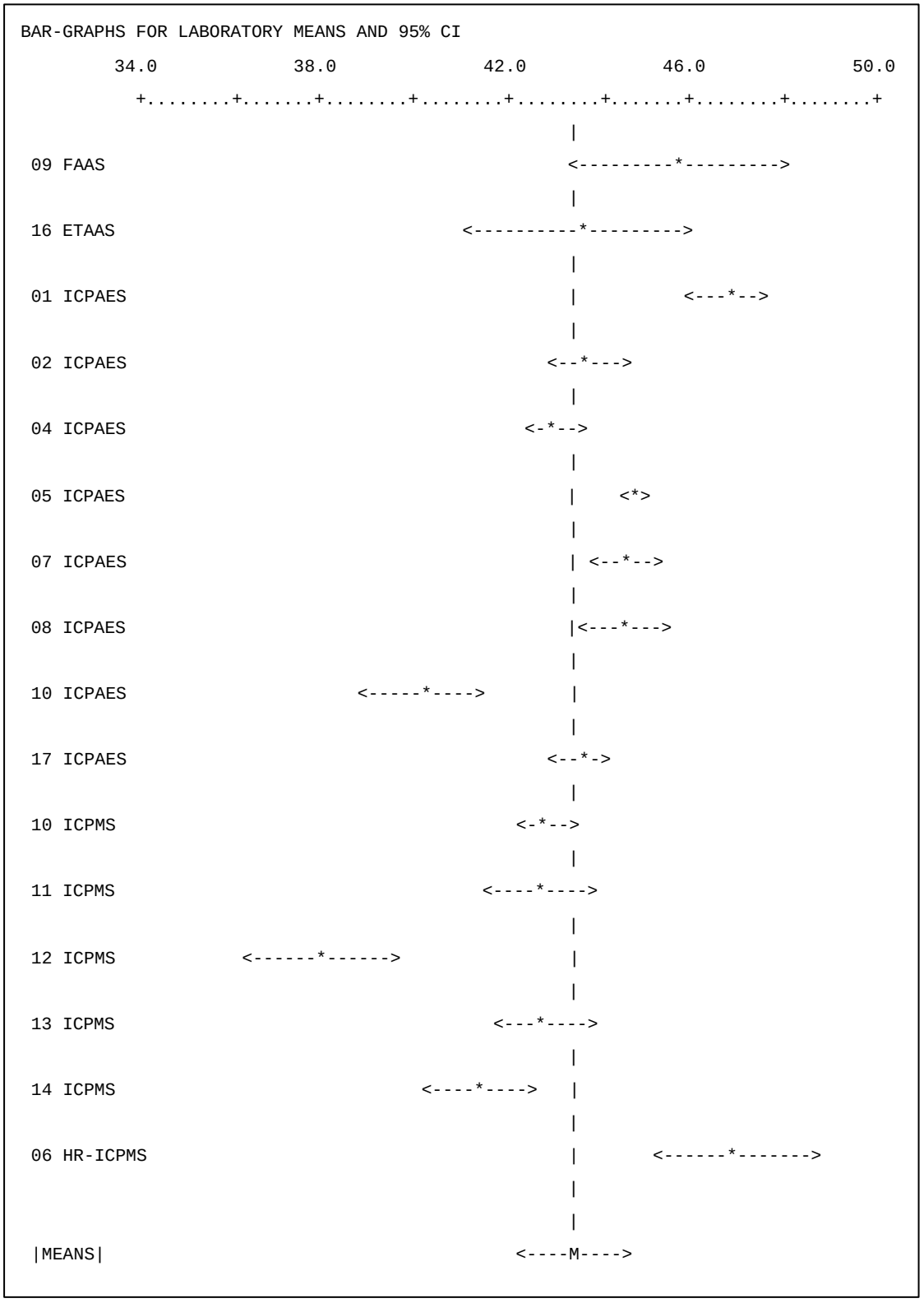

Figure 16 - Manganese in BCR-713 in µg/L

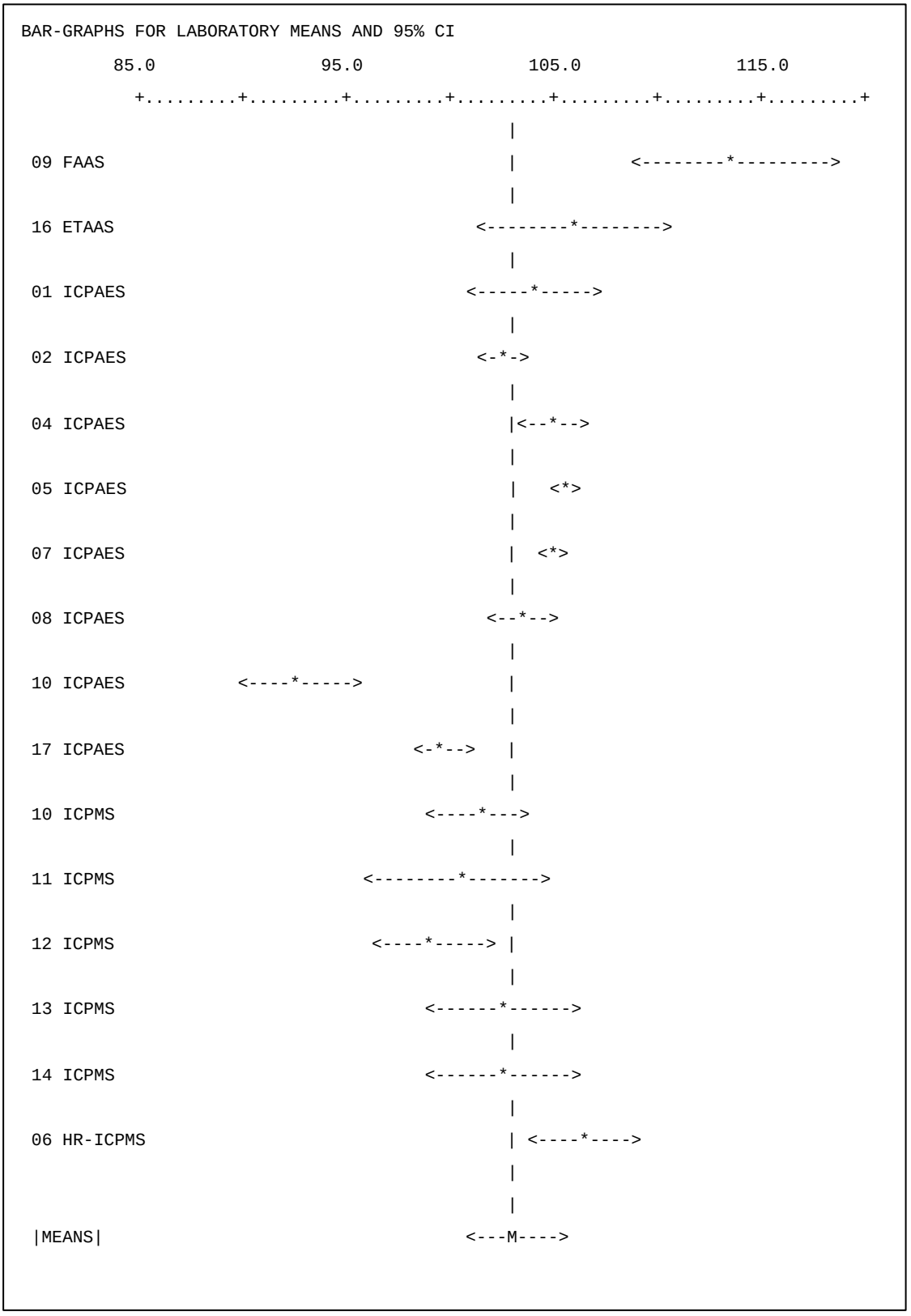

Figure 17 - Manganese in BCR-714 in µg/L

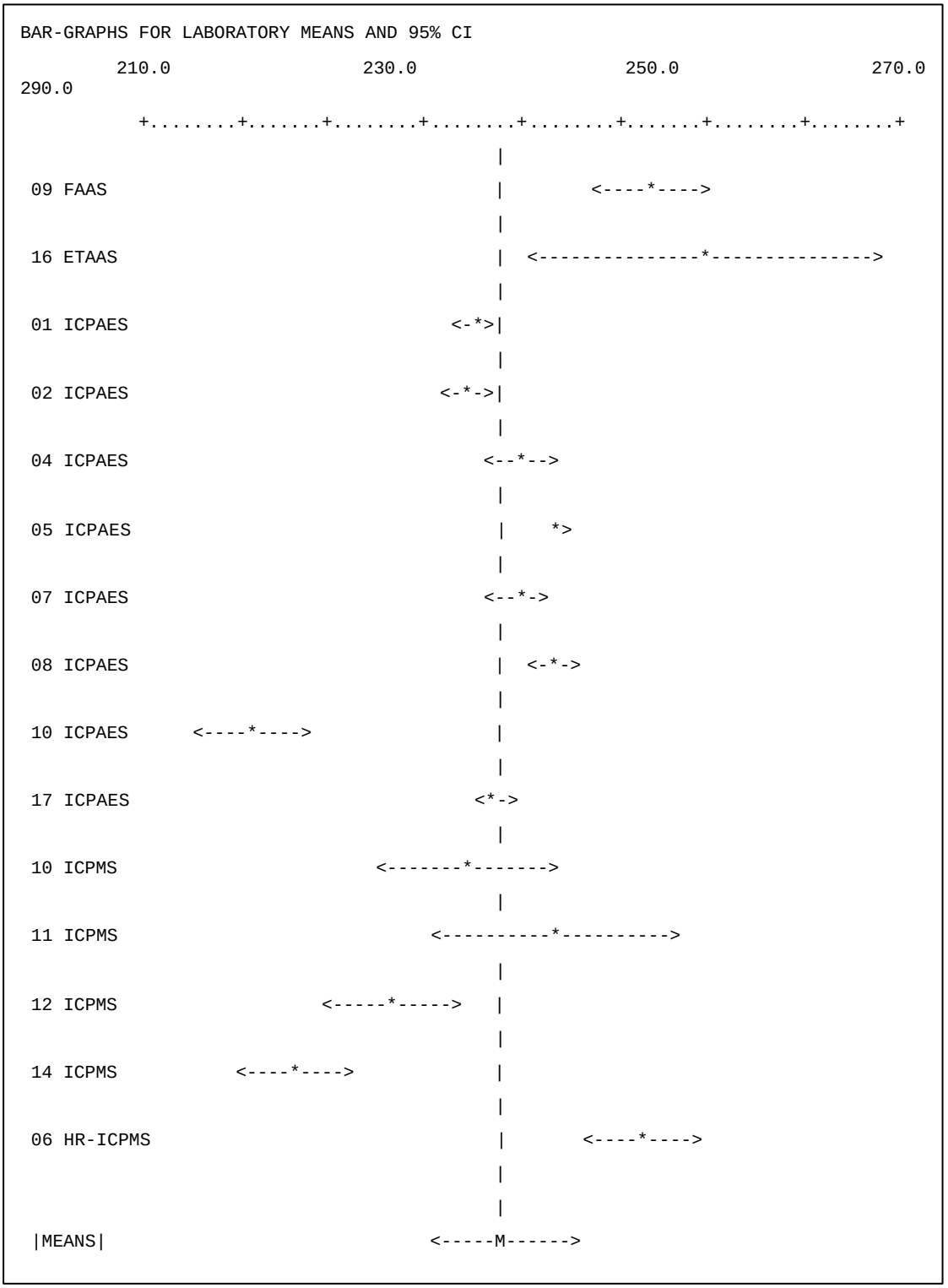

Figure 18 - Manganese in BCR-715 in µg/L

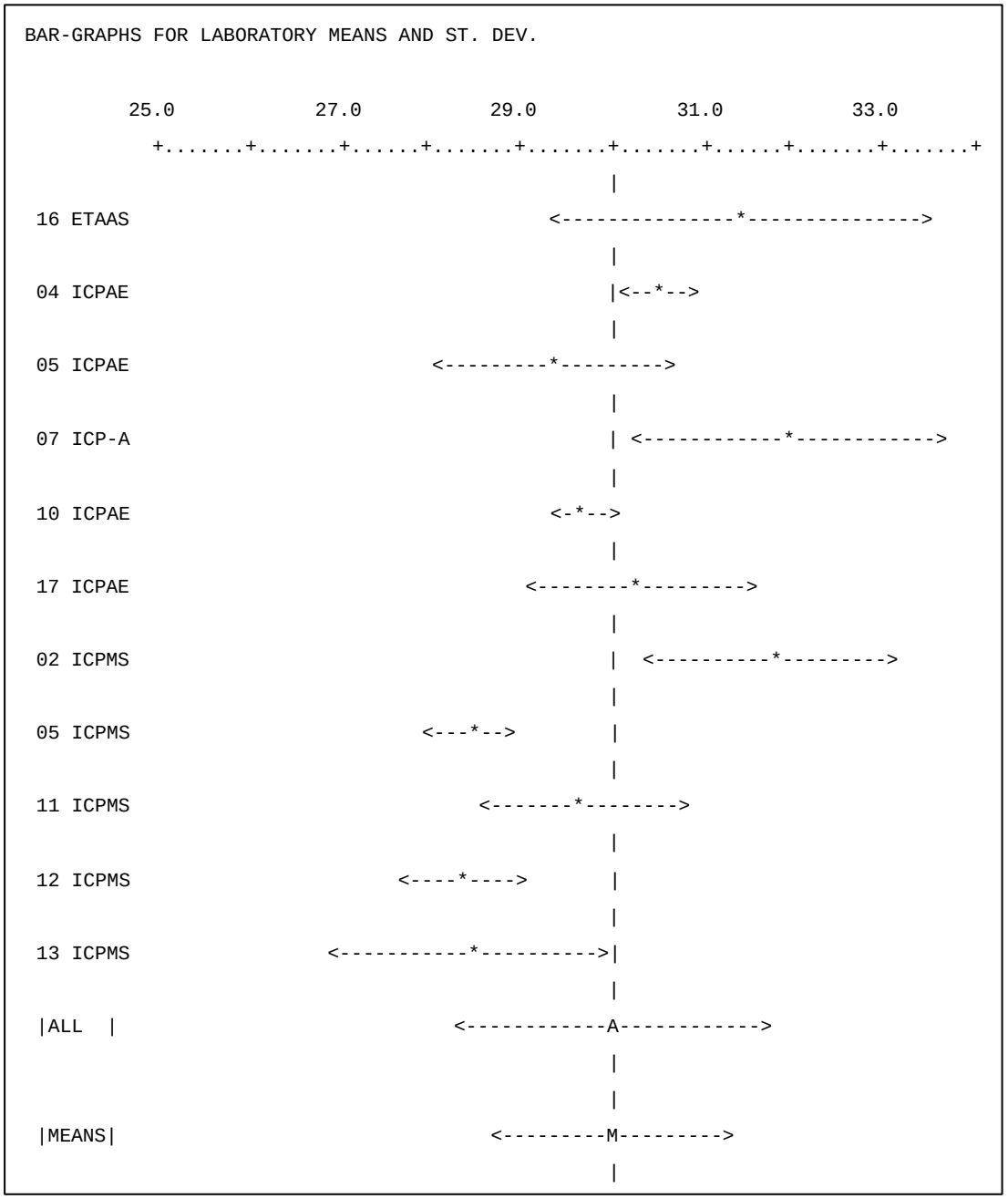

Figure 19 - Nickel in BCR-713 in µg/L

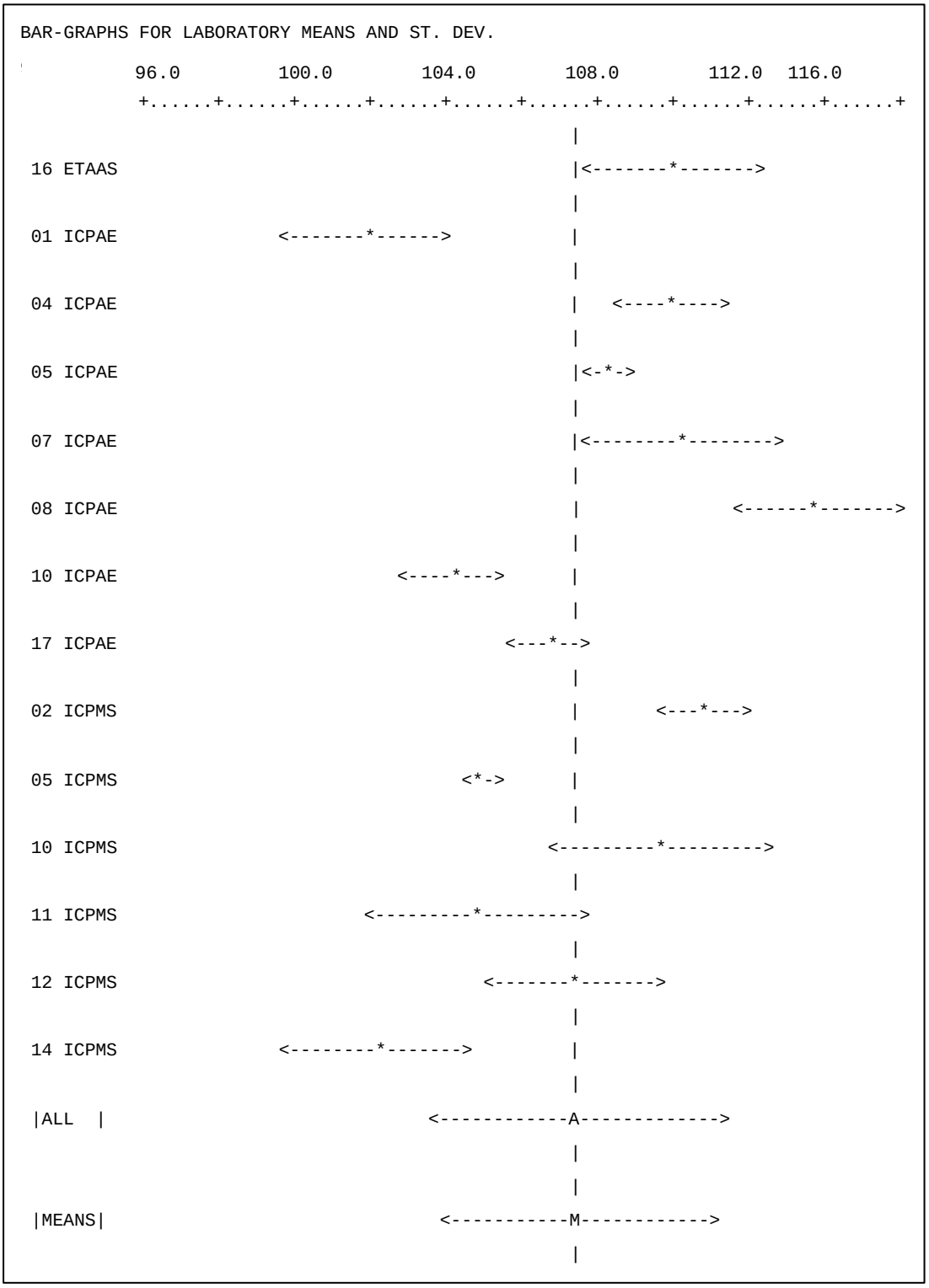

Figure 20 - Nickel in BCR-714 in µg/L

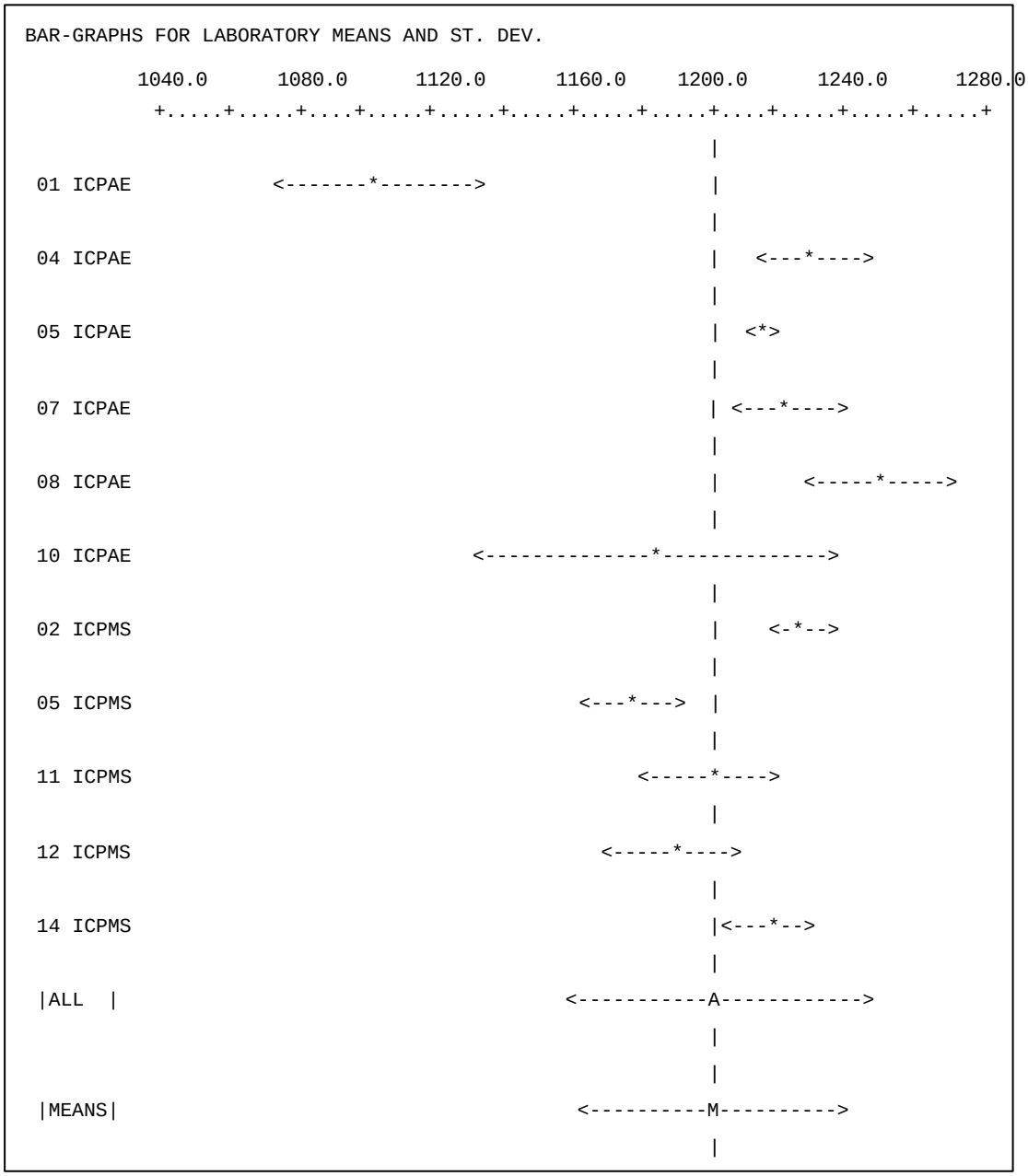

Figure 21 - Nickel in BCR-715 in µg/L

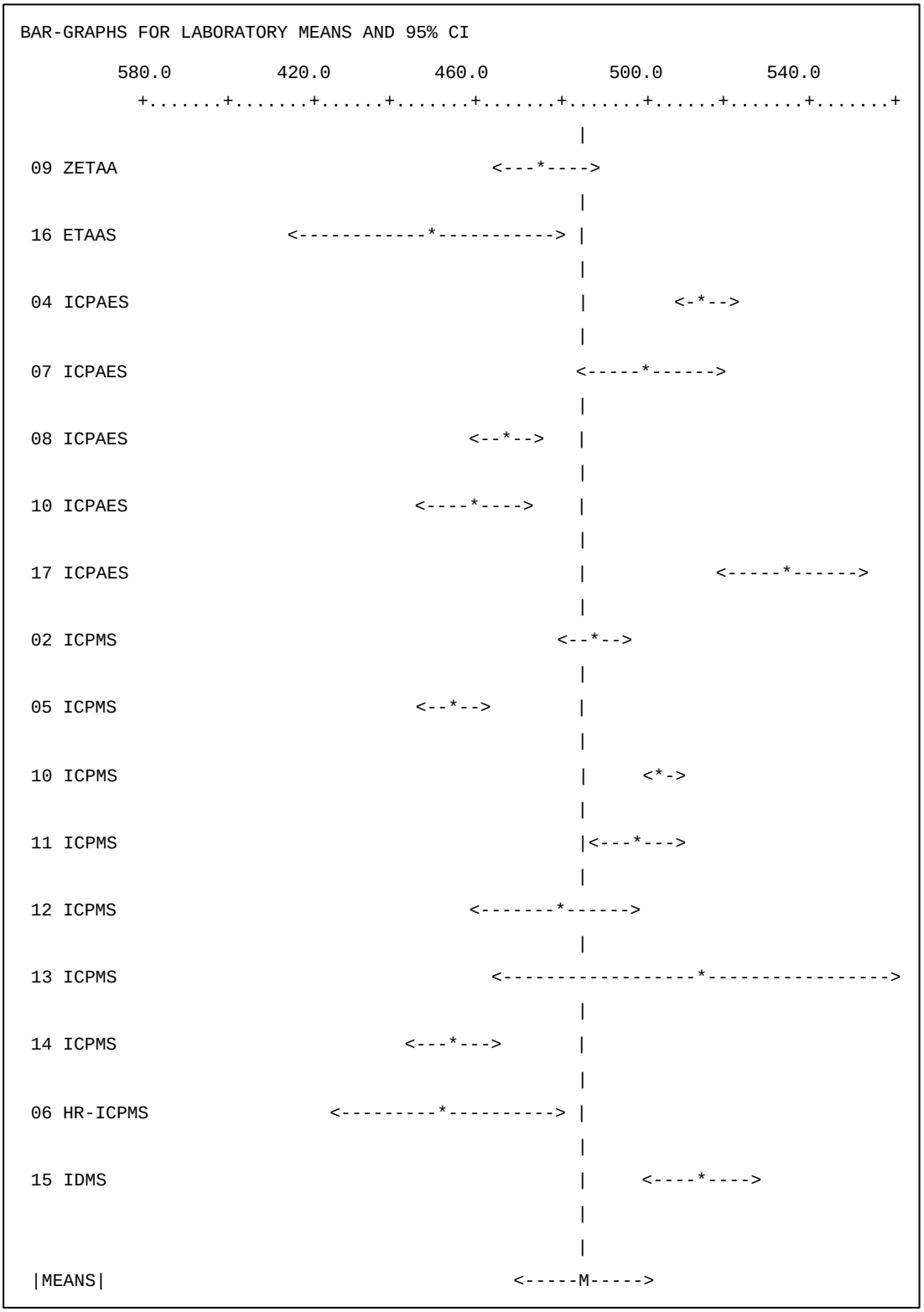

Figure 22 - Lead in BCR-713 in µg/L

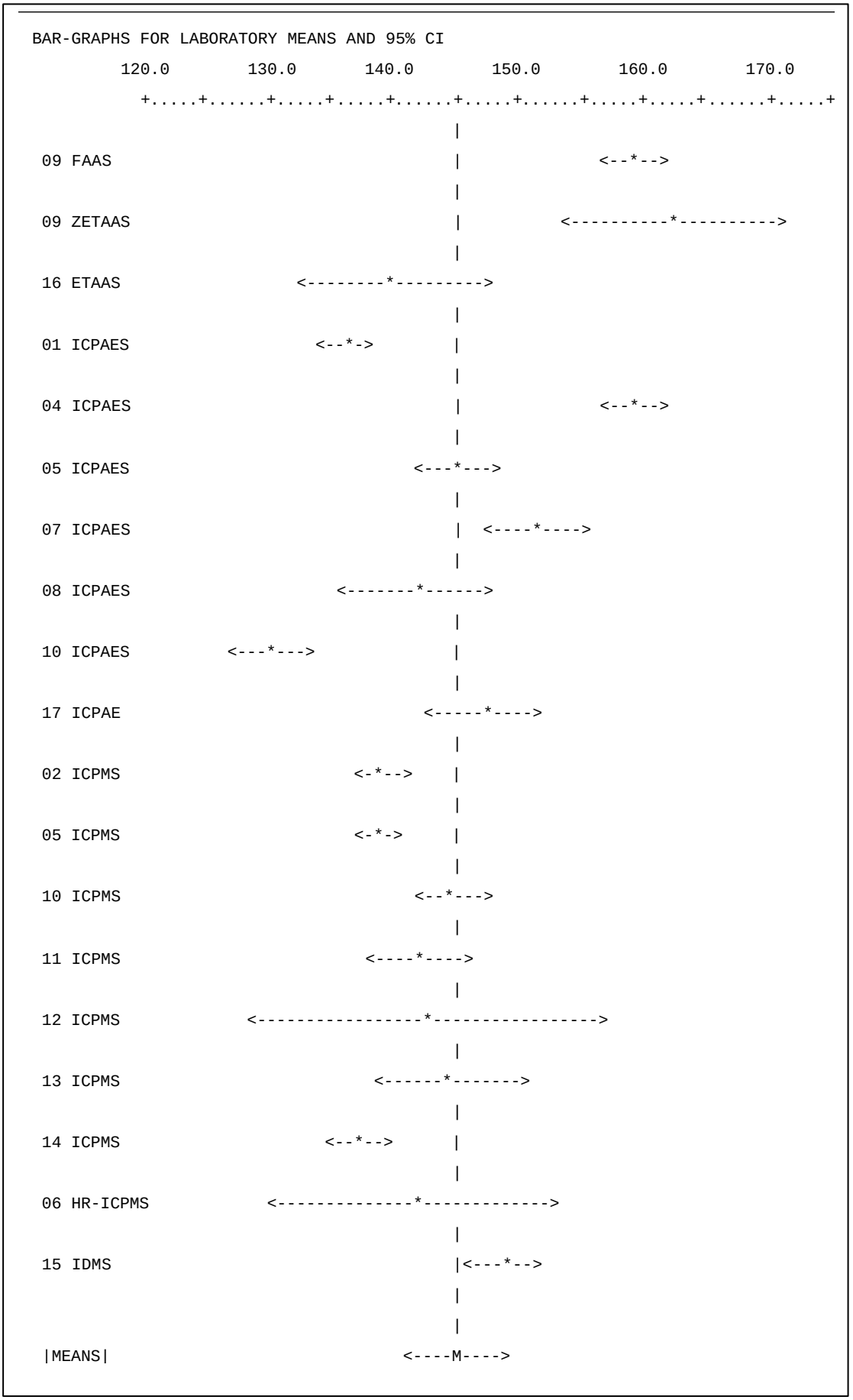

Figure 23 - Lead in BCR-714 in µg/L

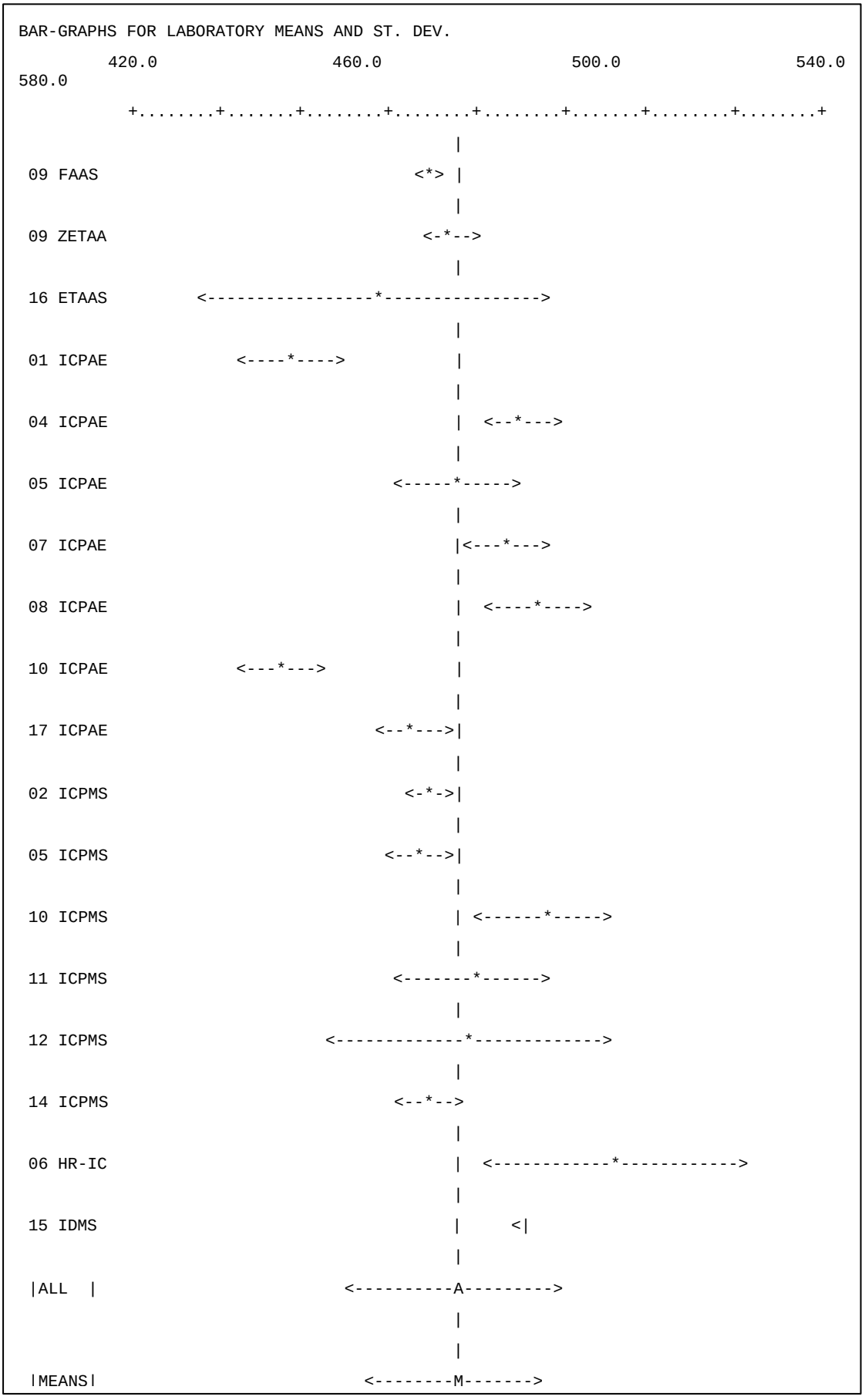

Figure 24 - Lead in BCR-715 in µg/L

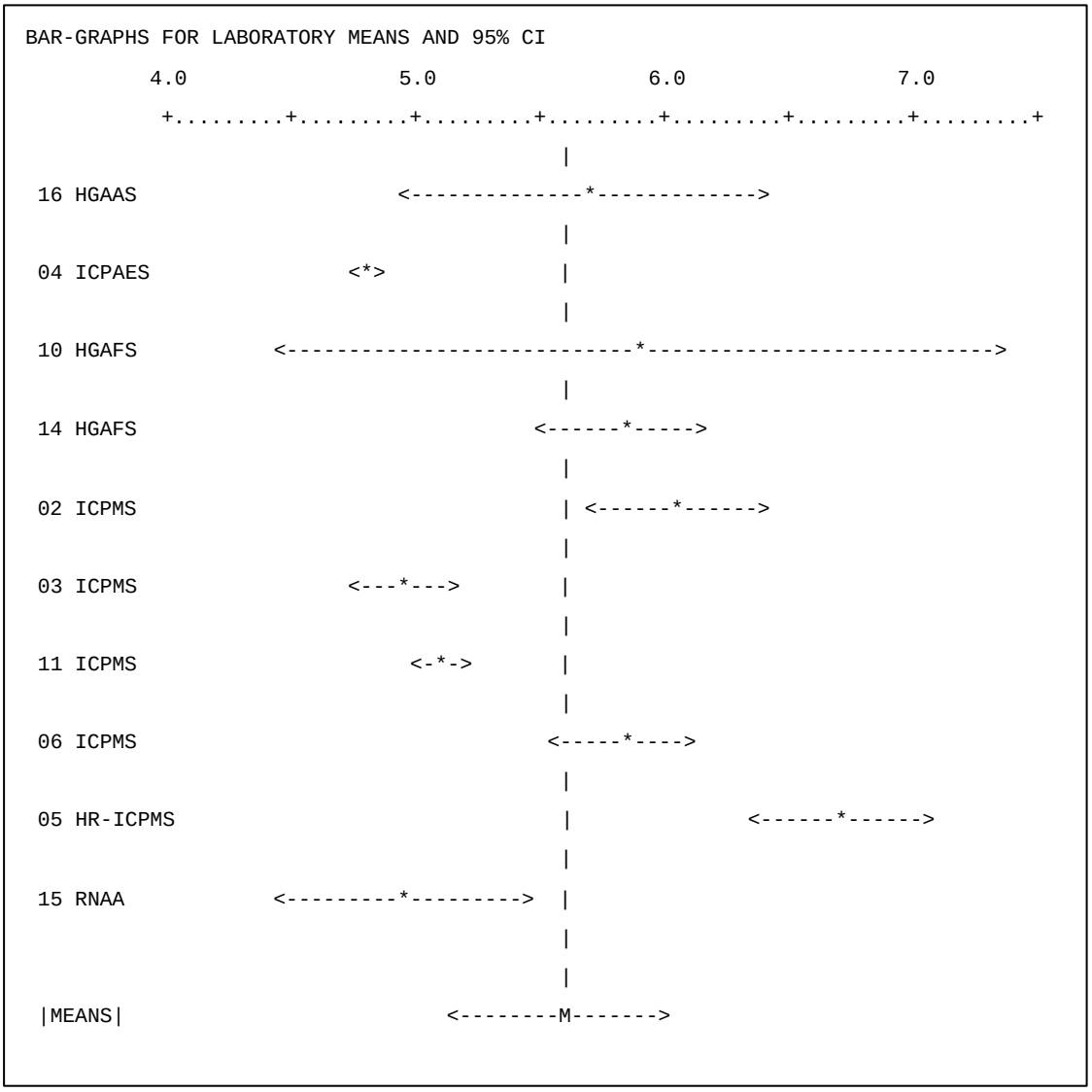

Figure 25 - Selenium in BCR-713 in µg/L

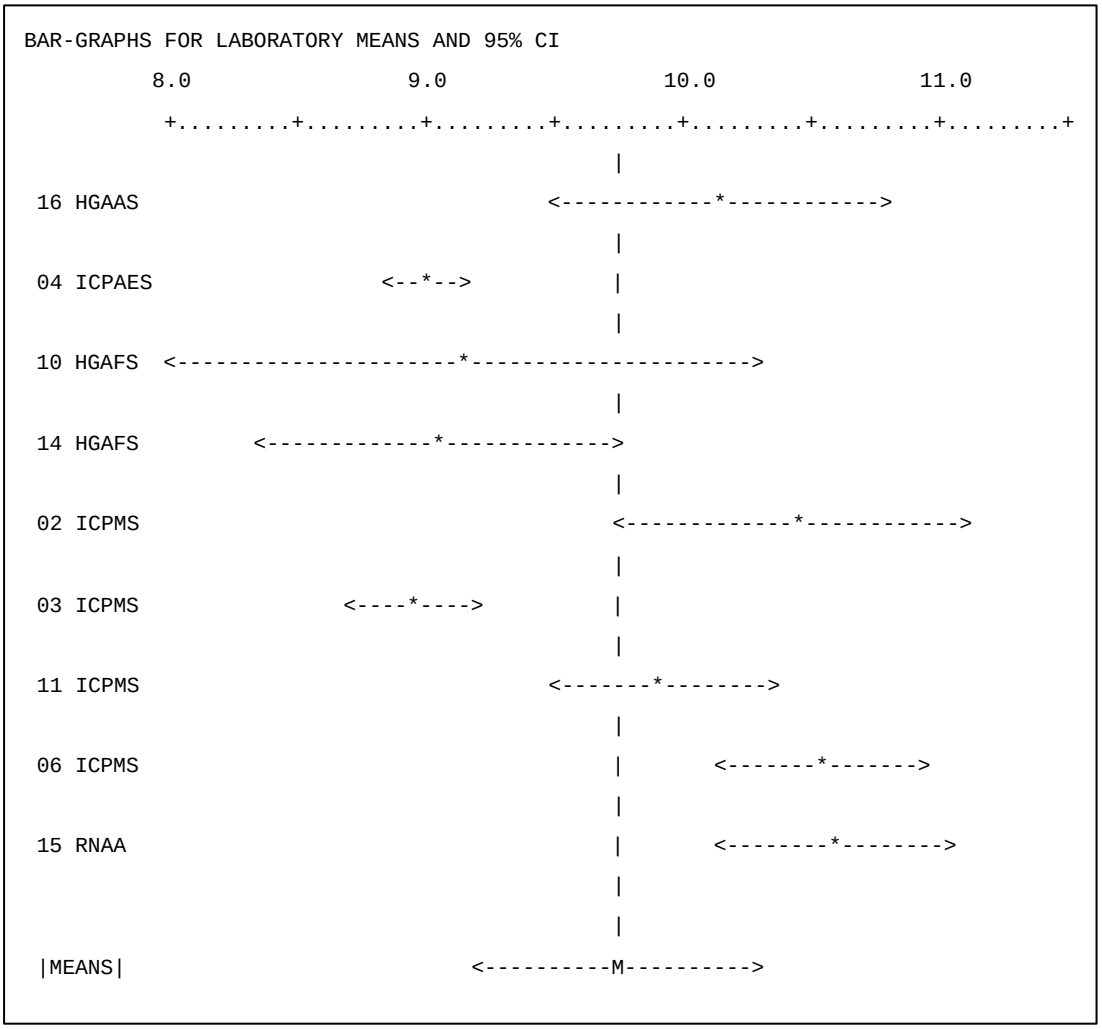

Figure 26 - Selenium in BCR-714 in µg/L

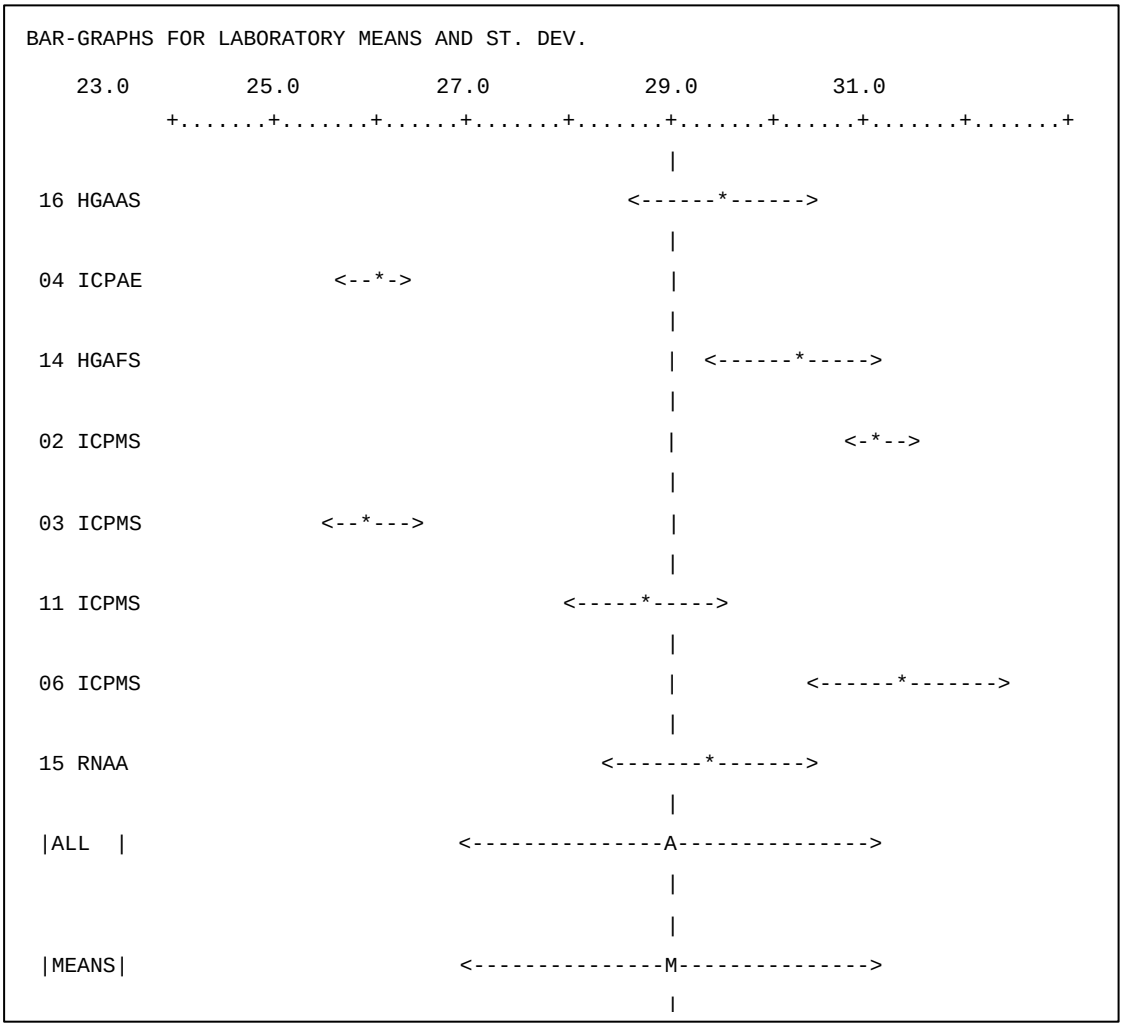

Figure 27 - Selenium in BCR-715 in µg/L

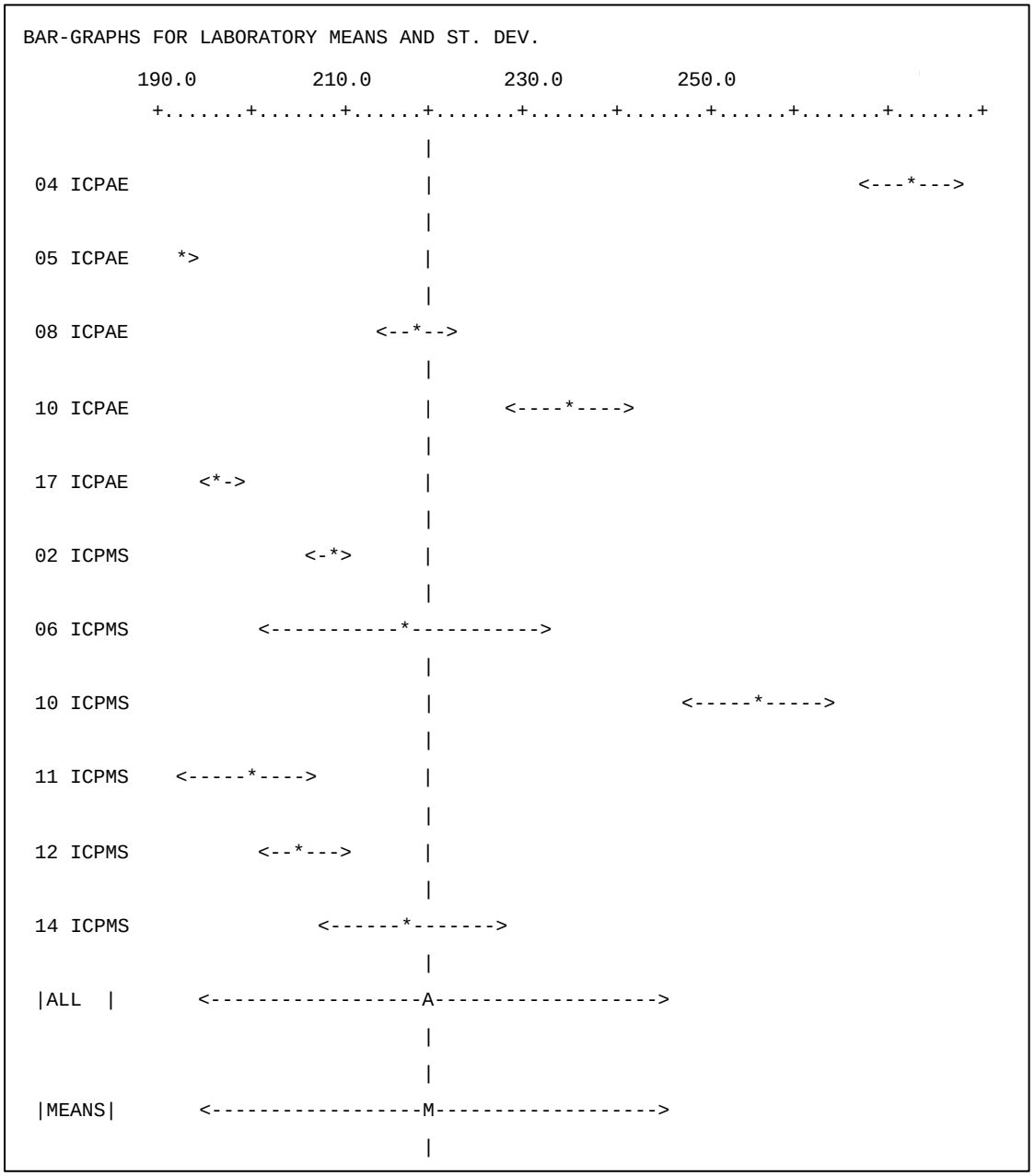

Figure 28 - Zinc in BCR-713 in µg/L

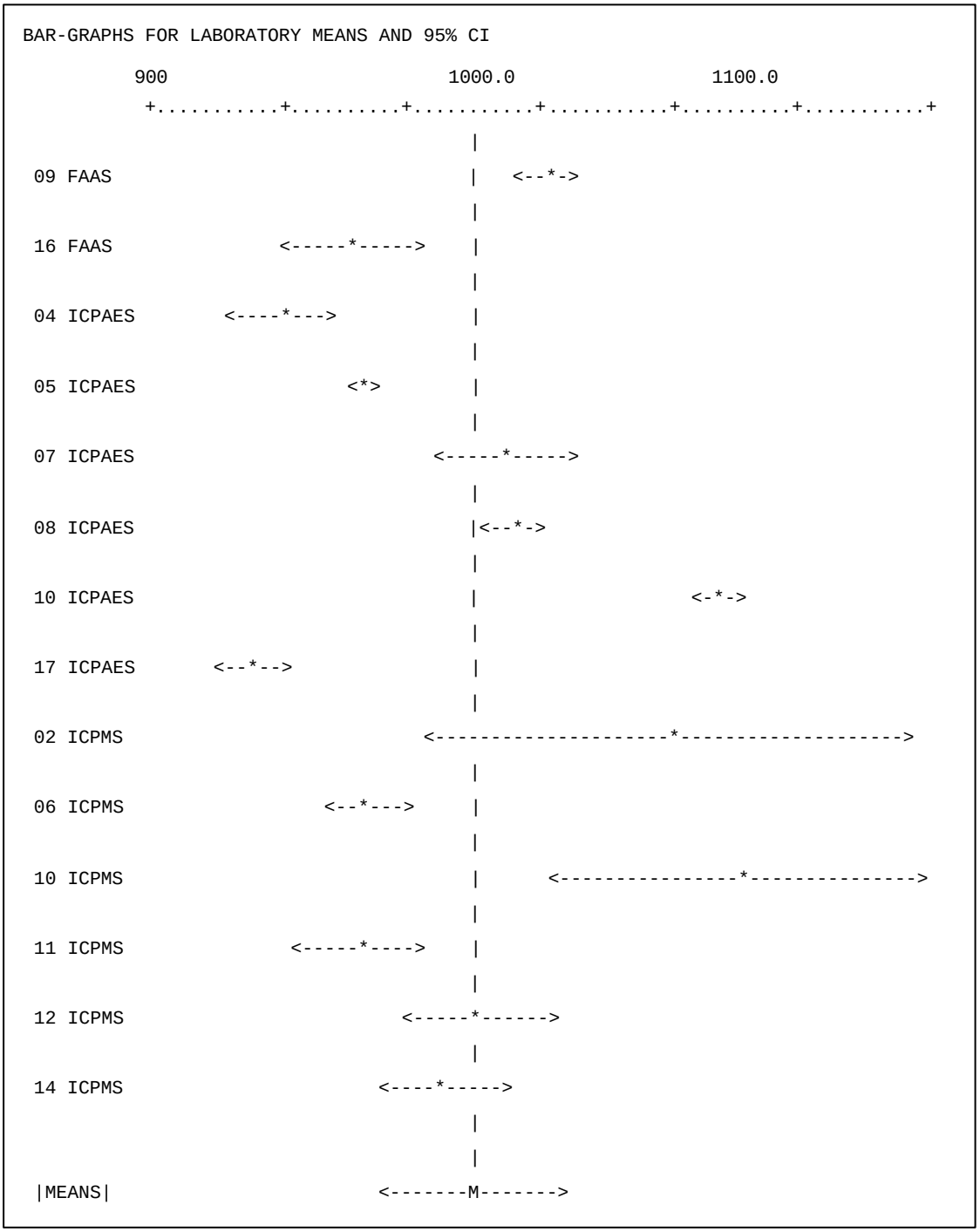

Figure 29 - Zinc in BCR-714 in µg/L

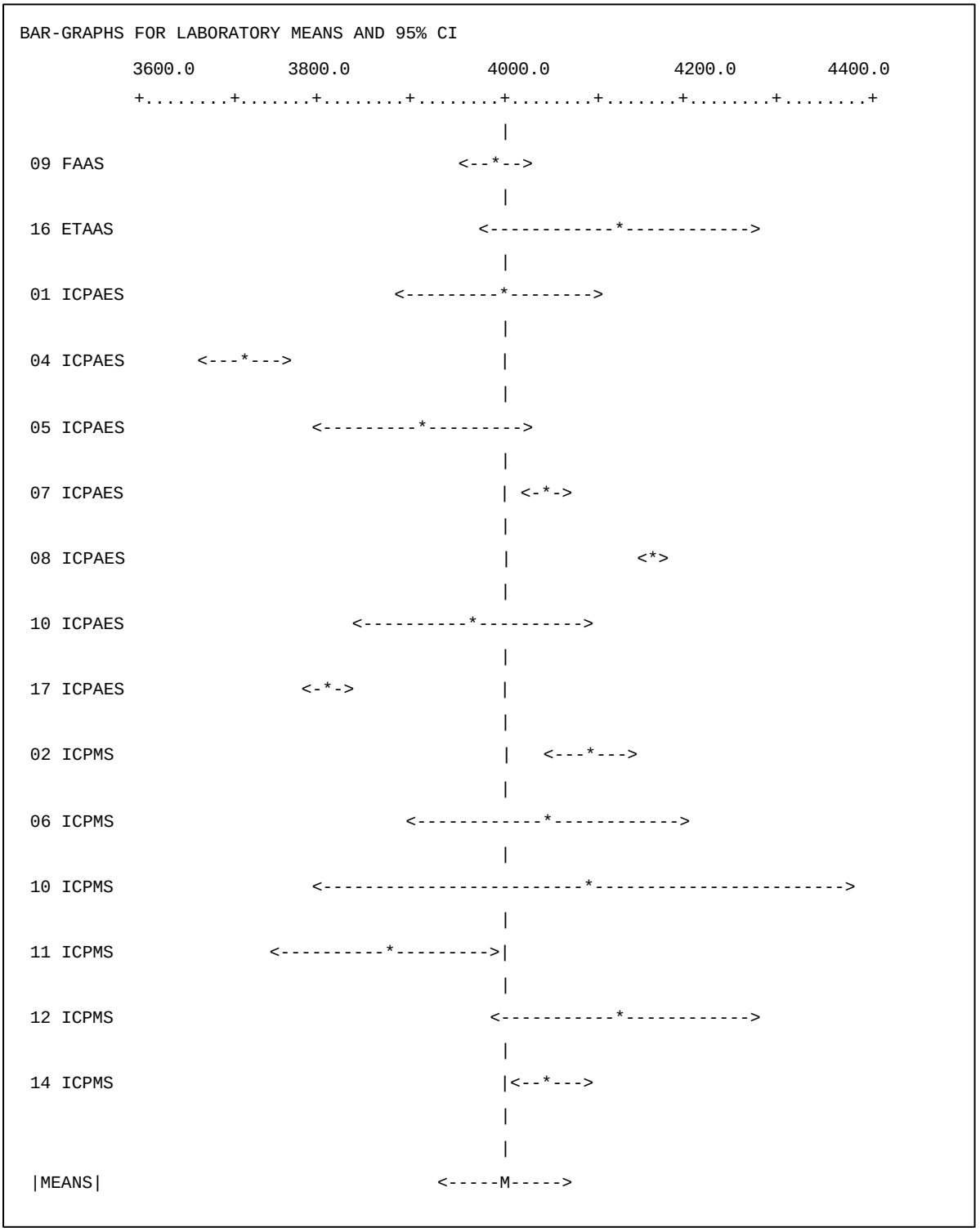

Figure 30 - Zinc in BCR-715 in µg/L

European Commission

EUR 21067 – DG Joint Research Centre, Institute for Reference Materials and Measurements –
The certification of the mass concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in wastewater, BCR-713 (effluent wastewater), BCR-714 (influent wastewater), BCR-715 (industrial effluent wastewater)
Authors: M. Segura, Y. Madrid, C. Cámara, C. Rebollo, J. Azcarate, G.N. Kramer, B.M. Gawlik, A. Lamberty, Ph. Quevauviller, S. Bowadt
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Abstract

This report describes the preparation of three spiked natural wastewater certified reference materials, i.e BCR-713 (effluent wastewater), BCR-714 (influent wastewater), BCR-715 (industrial effluent wastewater), the homogeneity and stability studies and the analytical work performed for the certification of the contents of selected trace elements. The report contains all the results and gives the methods used to certify the contents of the elements: As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in the three wastewater reference materials.

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